AD-A110 917   GENERAL TECHNOLOGY APPLICATIONS INC ARLINGTON VA   F/G 21/4
               INVESTIGATION OF THE APPLICATION OF A CRYOGENIC BLENDING PROCES--ETC(U)
               JAN 82 A F HADERMANN, P WATERS, J C TRIPPE   DAAK70-81-C-0134
UNCLASSIFIED   GTA-A-001   NL

1 OF 1
AD A
110917

END
DATE
FILMED
03-82
DTIC

LEVEL

INVESTIGATION OF THE APPLICATION OF

A CRYOGENIC BLENDING PROCESS TO

PRODUCE ANTIMISTING DIESEL FUELS

FINAL REPORT

by

Dr. A.F. Hadermann

Dr. P. Waters

Mr. J.C. Trippe

Mr. W. Weitzen

prepared by

GENERAL TECHNOLOGY APPLICATIONS, INC.
1901 North Fort Myer Drive
Suite 1015
Arlington, Virginia   22209

41240?

under contract to

U.S. Army Mobility Equipment
Research and Development Command,
Fort Belvoir, Virginia

DTIC
ELECTED

FEB 1 6 1982

A

Disclaimer

DISCLAIMER

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
General Technology Applications, Inc. 1901 North Fort Myer Drive, Suite 1015 Arlington, Virginia 22209	Unclassified
	2b. GROUP

3. REPORT TITLE

Investigation of the Application of a Cryogenic Blending Process to Produce Antimisting Diesel Fuels

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

Dr. Albert F. Hadermann   Mr. Jerry C. Trippe
Dr. Paul Waters   Mr. William Weitzen

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
January 15, 1982	64	10

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DAAK70-81-C-0134	GTA-A-001
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Distribution of the document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U.S. Army Mobility Equipment Research and Development Command, Fort Belvoir, Virginia

13. ABSTRACT

Fire-resistant fuels have been investigated by the United States Army as a means of reducing the risk of fire in land combat vehicles and certain aircraft. One approach has been the use of high-molecular-weight polymer additives for suppression of mist formations. The polymers which are effective in mist suppression are very difficult to dissolve in fuel. A newly discovered process for dissolving high-molecular-weight polymers is investigated to determine its applicability to the preparation of mist suppression fuels. The conclusions are that certain high-molecular-weight polymers which show strong mist suppression behavior can be dissolved rapidly in diesel fuel and that the new dissolving process appears to be adaptable to field use.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

FOREWARD

This report was prepared by General Technology Applications, Inc., under Contract No. DAAK70-81-C-0134. The project was administered by the Fuels and Lubricants Division, Energy and Water Resources Laboratory, US Army Mobility Equipment Research and Development Command, Fort Belvoir, Virginia. Mr. F.W. Schaekel served as Project Monitor.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

Fire resistant fuel for ground vehicles would reduce the threat
of fire to vehicles and personnel. The fuel must achieve a
reduction in the fire hazard while presenting minimum adverse
effects upon vehicle performance. In addition, the fire resis-
tant fuel must not present impractical logistic constraints in
terms of blending and transportation requirements, and storage
stability.

Six generations of fire resistant fuels have proved effective
for reducing fuel flammability hazards for either aircraft or
ground equipment, or both (reference (1)). These formulations
investigated by the U.S. Army included the following:

1. Fuel gellation;

2. Semisolid fuel-in-water emulsions;

3. Viscous-liquid, fuel-in-water emulsions;

4. High-molecular-weight polymer additives for suppres-
   sion of mist formations;

5. Volatile halogenated fire suppression fuel consti-
   tuent; and

6. Non-viscous, water-in-fuel, fire-resistant fuel
   emulsions.

Although each of these six approaches presented disadvantages,
the non-viscous, water-in-fuel emulsion system has shown the
desired fire-resistance while appearing to be most suitable
and practical. Use in the field, however, presents logistic
problems centering on the need for an emulsifying agent and
the need for large quantities of relatively pure water.

In view of the logistic problems with the water-in-fuel emul-
sion fuels, recent developments in the state of the art in
blending (reference (2)) and the introduction of turbine
powered battle tanks, the present project was initiated to
reappraise the fourth approach, "High-molecular-weight poly-
meric additives for suppression of mist formation." This
approach also may be promising for formulation of fire-resis-
tant fuels for U.S. Army helicopters and fixed wing aircraft.

A major problem associated with the high molecular weight poly-
mer approach in the past related to the difficulties in dissol-
ving these polymers in fuel. Existing dissolving processes
were slow and attempts to speed the process by vigorous mixing
degrade the polymers so that they are less effective in mist
suppression.

In 1978, General Technology Applications, Inc., made the discovery that some high molecular weight viscoelastic polymers can be dissolved virtually instantaneously under cryogenic conditions. The process, covered by a U.S. patent application, (reference (3)) involves grinding the polymer at liquid nitrogen temperature, activating the polymer particles through macroradical formation (references (4-6), followed by quenching the cold powder in solvent at ambient temperature. This blending method offers virtually instantaneous solvation with minimal degradation of mist suppression effectiveness.

Under Contract No. DTFA03-80-C-00070 from the Federal Aviation Administration, General Technology Applications, Inc. successfully applied this cryogenic method to blend polyisobutylene-JET A fuel solutions at the rate of approximately 4 gallons per minute at 3000 ppm. These solutions were tested for mist suppression behavior by the FAA and found to be superior at like concentrations to the currently investigated antimisting fuel.

As noted above, a major objection to the use of high-molecular-weight mist suppression additives has been the difficulty of dissolution. As presently conceived the GTA process can be used to blend dry polymer with diesel fuel forming antimisting fuel on demand and as required for vehicles at the pump. Using this process there would be no need to store polymer solution concentrate for blending with fuel nor would large holding tanks be required while the antimisting additive is being dissolved in the fuel.

The capability to blend antimisting fuel directly in the fuel tanks of military vehicles, could give military decision-makers the option to use it only when necessary, with minimal disruption to military operation. The fuel could be used only under battle and training conditions if so desired. In addition field control of polymer concentration could provide flexibility in tailoring fire protection to vehicle type and specific battle field conditions and requirements.

II. OBJECTIVES

The primary objectives of this investigation are as follows:

1. **Determine if antimisting polymer candidates can be blended in fuel.**

    GTA, Inc., was to apply its cryogenic solution making process to a series of polymer candidates obtained from the project officer (reference (7)). The polymers supplied to GTA included the following: Natsyn (Goodyear Tire and Rubber Co.), EPCAR 307 and EPCAR 5465 (Goodrich Chemical Co.), 10955 (Firestone Tire and Rubber Co.), L-130 (Exxon) and 2177-14 (U.S. Army (AMMRC)).

    In addition to the polymers obtained from the project officer, GTA also investigated three different molecular weight samples of polyisobutylene from BASF (B-100, B-200, and B-250), and proprietary polymers from Gulf, Shell and ARCO.

2. **Determine blending in two diesel fuels.**

    GTA, Inc., was to determine if the solvation or blending process was influenced by the choice of referee or standard-lot DF 7225.

3. **Determine the effects of polymer molecular weight, chemical composition and concentration in fuel on the blending process.**

4. **Test each sample solution for antimisting and viscosity as functions of time after blending and polymer concentration.**

5. **Assess the stability of the resultant antimisting fuels.**

6. **Determine the minimum concentration required for antimisting.**

7. **Report the parameters for optimizing the blending process.**

8. **Prepare and deliver 5 gallon samples of each selected polymer/fuel candidate.**

9. **Determine the appropriate, size, weight, power requirements, etc., of a field unit, and assess the applicability of this process to the Army's Fire-Resistant Fuel Program.**

III. APPROACH

It has been shown that the cryogenic grinding of polymers with molecular weights in excess of 10^4 leads to the production of a powder that shows the presence of macroradicals (reference (4-6)).

During cryofracture, a small number of main-chains are broken. The evidence for this is obtained directly from the observation of the characteristic electron spin resonance signatures of several kinds of radical species produced by mechanical fracture of polymers at low temperature. These spectra have been reported for polyethylene, polypropylene, polytetrafluoroethylene, polybutadiene, polymethylmethacrylate, polyisobutylene, polystyrene, polyvinylacetate, polycarbonate, and several polyamides (reference (3)).

Primary radicals are not as stable as secondary and tertiary radicals. The primary radicals produced by the scission of polyethylene rearrange to secondary radicals at 77°K. Some polymers like polyisobutylene produce very stable, tertiary radicals directly upon scission of the main-chain. The two radicals formed by main-chain scission of polyisobutylene are shown below:

$$\text{(I)} \quad \text{R} - \text{CH}_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\text{C}}} \cdot \quad + \quad \cdot \text{CH}_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\text{C}}} - \text{R'} \quad \text{(II)}$$

| Stable at 77°K | Unstable at 77°C |
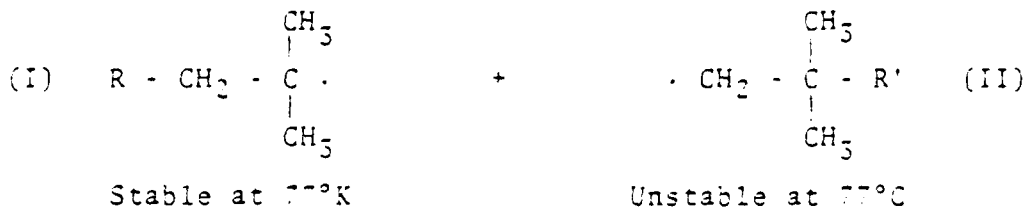
The macroradical designated (II) is stabilized by rearrangement to the following tertiary structure (III).

$$\text{CH}_3 - \text{CH}_2 - \overset{\displaystyle \cdot}{\underset{\underset{\displaystyle CH_3}{|}}{\text{C}}} - \text{R'} \quad \text{(III)}$$
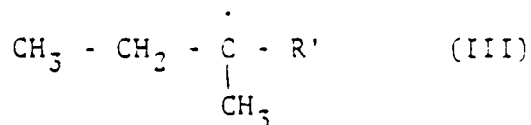
The radicals, I, II and III are also capable of abstracting H., resulting in migration of radical activity to other locations in neighboring macromolecular chains.

ESR investigations of ball-milled polymers reveal that the radical activity of the resultant powder depends on the polymer type, the molecular weight, and the particle size. A molecular weight of at least 10^4 is required before main-chain scission, rather than the simple intermolecular slippage, is observed.

Polymers with strong auto-adhesion, like nylon 66, tend to pro-
duce more radicals per gram under similar grinding conditions
than polymers with weaker intermolecular forces.

Unless cryofracture is pushed to very small particle sizes, the
number of main-chains broken will be a small fraction of the
total number of molecules present. Apparently, the small amount
of degradation accompanying cryofracture to the range of parti-
cle sizes available using GTA's hammer mills does not unduely
affect the antimisting performance of the polymer candidates
tested during this project.

Although the production of macroradicals by mechanical fracture
has been known since 1959 (reference (9)), the rapid solvation
phenomenon was not reported prior to 1979 (reference (2)).

Basic research into the nature of the rapid solution process is
currently being investigated, and the results will be presented
in 1982 (reference (1)). Several mechanisms are plausible, but
the one with the best basis in past data revealed through inves-
tigations of radical-molecule interactions involves the reaction
of macroradicals with some solvent molecules to enhance solvation.

It is also possible that the presence of macroradicals changes
the nature of the physical interaction between the high-energy
surface and neighboring solvent molecules. This could affect
the balance between molecule-molecule- and molecule-solvent
interactions with a concomitant increase in the rate of solution
by a purely physical process. It is also possible, of course,
that both physical and chemical interactions work together to
increase the rate of polymer solution.

The practical approach used in the present project was to
develop apparatus for cryogrinding polymer samples and causing
the active particles to impinge directly onto the surface of
flowing fuel. This approach was used to minimize decay time
after forming the macroradicals and to promote separation of
the polymer particles in nitrogen gas prior to meeting the
fuel surface. The apparatus and test methods are described in
detail in the next section.

IV. EXPERIMENTAL

A. DESCRIPTION OF APPARATUS AND PROCEDURES

The following section is devoted to describing the apparatus and test methods used to obtain the data reported in the next section.

1. Spex Hammer-Cutter Mill and Fuel Blender.

The small apparatus shown in Figure 1 was designed for use with small polymer samples. It was imperative that a small grinder/blender be available for preparing small samples of anti-misting fuel from some experimental proprietary polymers available only in limited supply.

The basis of the small system is a Spex Model 5200 Analytical Hammer-Cutter mill with a 0.5 mm screen. The screen was backed with a polyethylene adaptor to prevent large particles from bypassing the holes. This corrected a design deficiency in the screen as supplied from the vendor.

The top of the mill was drilled, tapped and fitted with a 1/8" NPT male tubing adaptor that was connected to an insulated liquid nitrogen reservoir via an insulated polyethylene tube of 1/4" I.D. The reservoir was fitted with a tapered, solid polyethylene rod for adjusting the flow of liquid nitrogen to the mill.

Polyurethane was foamed in place to insulate the mill and the liquid nitrogen delivery line. The mill face plate was separately insulated to permit ready access to the mill for cleaning. The hopper lid on the top of the hinged face plate was removed and a carefully carved and fitted styrofoam block containing the polymer reservoir was mounted on it. The structure of the polymer reservoir is shown in Figure 2.

The polymer/solvent blending chamber is shown in Figure 1. The unit was constructed by welding a polyethylene funnel to the bottom of a polyethylene bottle of the same diameter (7"). A solvent inlet and a solution outlet were located 180° apart near the bottom of the chamber so as to maintain a liquid depth of approximately 3/8" under continuous solvent flow. To relieve gas pressure at the output of the mill, a downward angled nitrogen gas vent was welded on the cone as shown.

A 15 gallon polyethylene carboy was modified to produce a constant-head Mariotte bottle to supply solvent to the blending chamber at a constant rate. The rate was adjustable

FIGURE 1

SPEX HAMMER-CUTTER MILL AND FUEL BLENDER

- Mariotte Bottle
- Diesel Fuel Supply
- Liquid Nitrogen Flow Control Rod
- Liquid Nitrogen
- Liquid Nitrogen DEWAR
- Polymer Reservoir (See Figure 2)
- Needle Valve Flow Control
- Insulated Liquid Nitrogen Line to Mill
- Foamed Mill Insulation
- Spex Mill
- Teflon Stopcock
- Timer
- Temperature Probe
- -150.0
- Temperature Readout
- Insulated Adaptor Sleeve
- N₂ Vent
- Polyethycene Blending Chamber
- Polymer Solution

FIGURE 2

POLYMER RESERVOIR- CROSS SECTION

FIGURE 2 — POLYMER RESERVOIR- CROSS SECTION

Polyethylene Inner Container

Insulated DEWAR

Solid Polyethylene Stopper Rod

Spacer

Liquid Nitrogen

Carved Foamed Polystyrene Block to Fit Mill Hopper

Mill Hopper

Polyethylene Feed Tube - 3/8" I.D.

via an inline, stainless steel needle valve left open to a pre-established number of turns. Rapid starting and stopping of fuel flow was accomplished by opening or closing an inline teflon stopcock.

A 1/8" diamter hole was drilled into one side of the end tubulation at the exhaust of the mill. The immersion probe of a Caspar Model DPT-600 platinum resistance thermometer was placed in this hole to monitor temperature during mill cooldown and the grinding/blending operation.

A typical run involves the introduction of 2 grams of polymer chunks (1/8" to 3/16" cubes) over 30 seconds. The solution is recovered in the collection flask. The solvent flow rate is preset to one liter/minute, resulting in the collection of approximately 500 ml of polymer-fuel solution.

2.   Bantam Hammer Mill and Fuel Blender

The apparatus shown in Figure 3 was designed for the preparation of 5 gallon samples of polymer/fuel blends. The mill was insulated in three separable sections using polyurethane foam. A conical adaptor was also insulated with polyurethane foam and fitted on the inside with a 60 degree, welded polyethylene sleeve to provide a smooth, relatively nonstick surface. The mill screen contained angled slots approximately 1 cm long with a width of 0.027" (0.686 mm). Unlike the screen used in smaller Spex mill, the slotted screen offered very little resistance to the passage of ground polymer powder thereby minimizing mill residence time and impact heating. The hammers in this mill, compared to the hammers in the Spex mill, each carry a single linear knife edge. Also, unlike the screen in the Spex mill, the slotted screen is designed to fracture particles rather than to merely function as a particle size selector.

The polymer chamber is adapted to fit into the hole at the top of the mill face plate. This container holds the polymer sample at the temperature of liquid nitrogen at one atmosphere pressure (70°K).

The blending chamber was fashioned from a rectangular polyethylene carboy fitted with 3/4" diameter tube fittings (welded in place). A circulating pump is used to provide a fresh solvent surface to the impinging powder stream during a grinding and fuel blending run. Using the 5 gallon fuel sample, the pump turns the fuel over only once during a one minute grinding and blending run. This assures minimal degradation during the solution process. The pump is of a wobble-plate rather than gear or centrifugal design, further minimizing possible degradation during blending.

FIGURE 3

BANTAM HAMMER MILL AND FUEL BLENDER
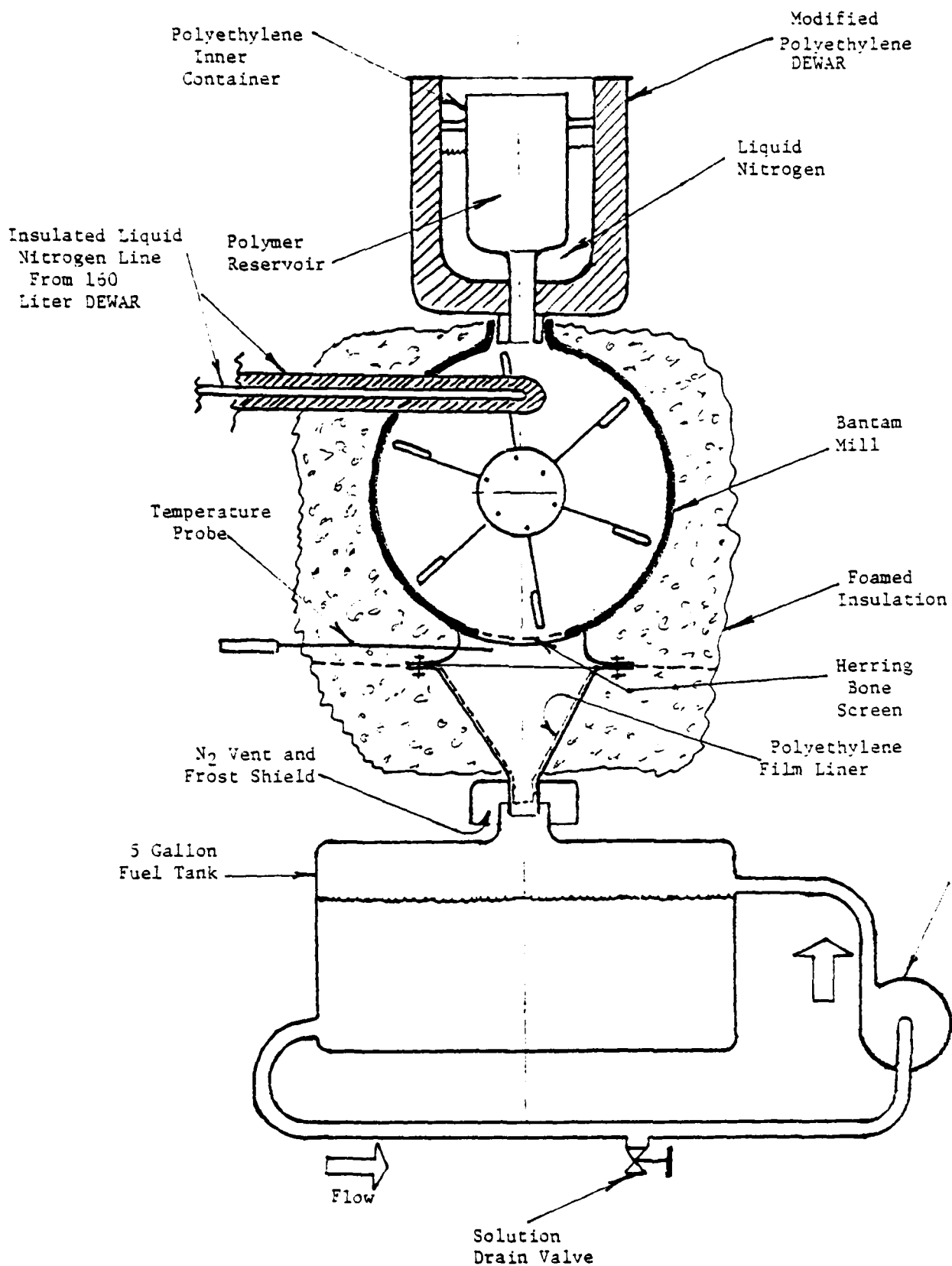
Prior to assembling the apparatus depicted in Figure 3, the pulley system was modified as suggested by the manufacturer to operate the hammer assembly at 7000 rather than 14,000 rpm. This minizes the tendency of the ground material to become entrained in the mill.

3. Antimisting Fuel Effectiveness Tester

The purpose of an antimisting fuel effectiveness tester is to provide quantitative data for determining the effect of molecular weight on antimisting and to determine how antimisting depends on polymer type and concentration. Initial attempts to determine or estimate the effectiveness of polymer solutions by photographing and subsequently analyzing the photographs proved to be too subjective to be of any value to the project. A simple quantitative antimisting effectiveness tester (Figure 4) was devised to provide quantitative gravimetric data related to mist generation.

A Burgess paint sprayer serves as the mist generator in the antimisting tester. The sprayer was mounted in a hole in one side of a 5-sided test chamber made out of wood framing and 1/4" particle board. A ringstand holding an inclined funnel (3" diameter) was located on a line with the axis of the sprayer. The lower edge of the funnel opening was positioned 9" from the orifice. The location and orientation of the inclined funnel were marked and retained throughout the antimisting test program.

The principle of operation of the tester is based on the observation that neat fuel leaves the orifice of the sprayer in a diverging, 3-dimensional fan pattern of very fine mist particles that disperse rapidly with increasing distance from the point of generation. In contrast to this, an antimisting solution leaves the orifice in a much narrower, more acute cone of coarse particles or strands, and in the upper limit of concentration exits as a coherent stream with little divergence and no attendant mist. Intermediate cases are observed as varying degrees of interception of ejected solution by the receiving cone collector.

A weighed sample of the solution to be tested is placed in a tared polyethylene beaker. A tared polyethylene beaker is also placed as shown in Figure 4 to capture the solution impinging on the open surface of the funnel. The sprayer, after a rinse with neat fuel, is operated for 60 seconds and the ejected material is collected in the receiving beaker. The amount of mist that is not recovered in the receiving beaker is simply P minus R where P is the decrease in mass of the solution at the sprayer and R is the mass gain of the receiving beaker. To correct for variations in pumping

FIGURE 4

ANTIMISTING FUEL EFFECTIVENESS TESTER

$$\text{FRACTION OF MIST} = \frac{P-R}{P}$$

Model V5860
Burgess Sprayer

Solution (P)
Beaker

a° (Fixed)

d
(Fixed Distance)

Stand

Collector
Funnel

Collected
Ejected
Material (R)
Beaker

5-Sided
Box
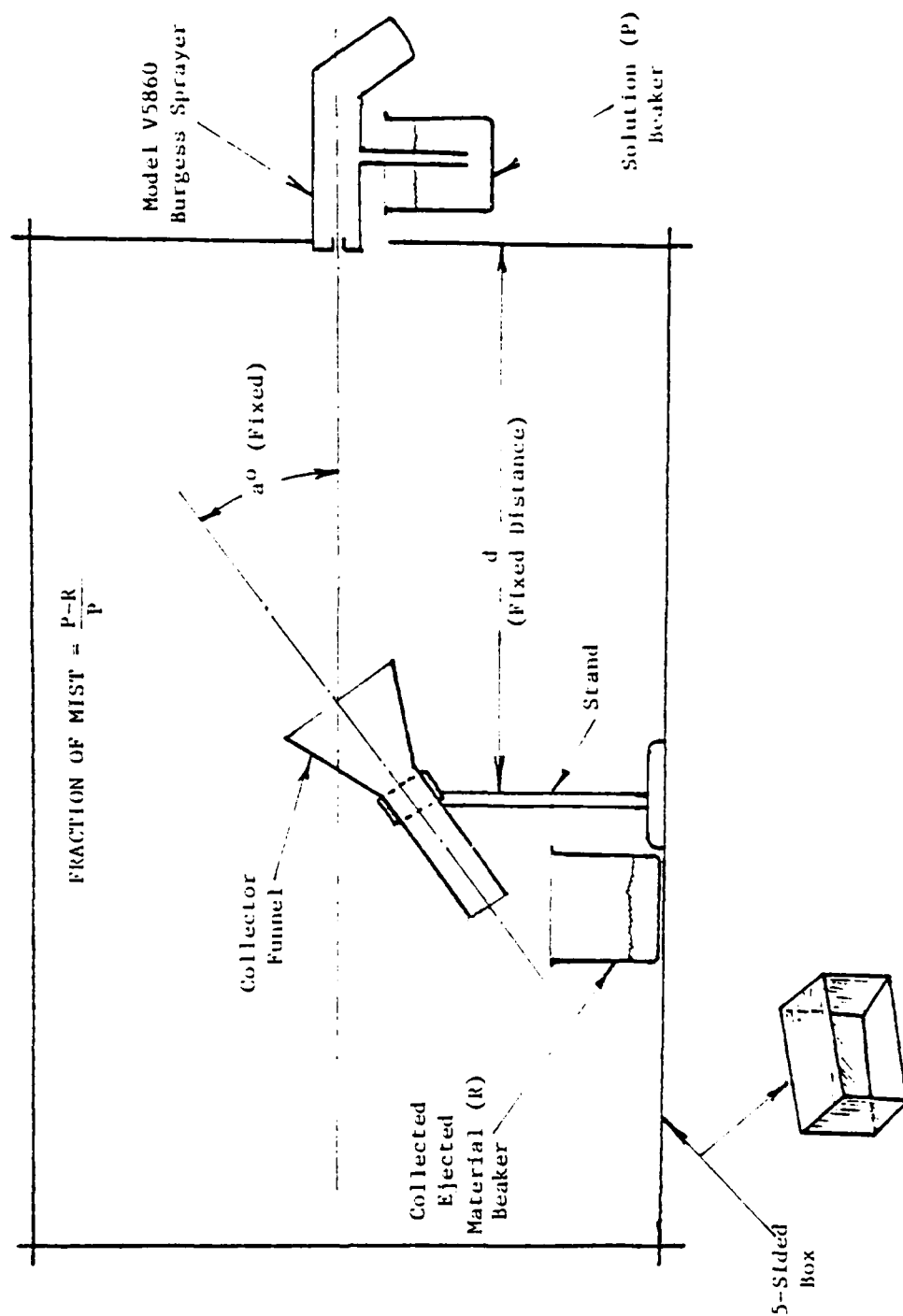
rate with solution viscosity and viscoelasticity the ratio (P-R)/P is taken as a measure of the misting per gram of solution pumped. When R is equal to P, (P-R)/P is zero, corresponding to zero grams of mist per gram of solution pumped. When R is zero, one gram of mist is produced by pumping and spraying of one gram of solution. It was found to be most convenient for extrapolation to plot the negative of the natural logarithm of (P-R)/P vs concentration in determining the relative antimisting effectiveness of different polymer/fuel blends prepared by cryogenic grinding/blending. The test was found to be suitable for application to cold solutions immediately after preparation. It was more useful for evaluating cold solutions than viscometry which required heating to 100°F. It was also found to be more sensitive to the presence of small amounts of antimisting polymers than dilute solution viscometry. This is evident in the analysis of the data presented in the next section.

Polymers selected on the basis of data developed using the GTA antimisting effectiveness tester (in consultation with the project officer) were then used to prepare 5 gallon lots of solutions in referee grade DF 7225 for engine performance and fire resistance testing by Army personnel.

This simple antimisting test concept does not supplant fire resistance testing. It is, however, suitable for determining the antimisting level of a solution immediately after preparation by cryogenic grinding and fuel blending. It is also extremely useful for determining the concentration dependence of the anti-misting behavior of a polymer/fuel system.

In the next section it is shown that most plots of antimisting vs concentration are linear in $-\ln(\frac{P-R}{P})$ vs concentration in weight percent. For the purpose of comparing the effectiveness of different polymers, linear regression analysis was used to obtain the correlation coefficient, slope and intercept of the line for each polymer-fuel system studied. The effectiveness of each polymer can be expressed as the concentration required to produce an antimisting system corresponding to the recovery of 95% of the material ejected from the sprayer. This corresponds to $-\ln(\frac{100-95}{100}) = MC_{5\% \text{ mist}} + b$ where m is the slope, $C_{5\% \text{ mist}}$ is the concentration in weight percent corresponding to recovery of 95% of the sprayed material in the recovery beaker and b is the intercept. Rearranging this expression and taking the natural logarithm of 0.05 leads to $C_{5\% \text{ mist}} = (2.996-b)/m$. Thus the antimisting effectiveness of different polymers in diesel fuel can be expressed on the same basis as the concentration required to achieve 95% recovery of the sprayed material. The method is suitable for determining the effectiveness of antimisting systems of both the cohesive, viscoelastic, nonrebounding fibrous type, e.g., polyisobutylene

and the less fibrous, large droplet type, e.g., the proprietary Shell polymer. This will be discussed in detail in the next section.

One other useful function can be constructed for each polymer system. The percentage of sprayed materials lost as mist is given by:

$$M = 100e^{-(mC + b)}$$

where $M = \%$ lost as mist in weight %, m is the slope and b is the intercept of the plot of $-\ln(\frac{P-R}{P})$ vs C, the concentration in weight percent. This function could be used in a future effort to link this gravimetric antimisting test procedure to required fire resistance values for specific degrees of protection required under combat conditions.

4. Determination of Concentration of Antimisting Solutions

Concentrations of polymer solutions in diesel fuel were determined by viscometry. Stock solutions of each polymer were prepared by weighing both polymer and solvent to achieve concentration in the range of 0.1 to 1.0 weight percent. The process of solution by conventional diffusion was monitored over a period sufficiently long to assure complete solution with minimal agitation. Agitation consisted of gently swirling the content of the flask for approximately 15 seconds a day while inspecting using a high intensity beam of light.

Each polymer stock solution was blended with neat fuel to prepare a series of solutions of different concentrations. Kinematic viscosities of each solution were obtained in triplicate at 100 ± 0.2 °F using certified, calibrated viscometers. Concentrations in weight percent were plotted against kinematic viscosity in centipoise for each polymer.

Calibration curves providing concentration from a measured viscosity were obtained for all polymers investigated with the exception of Epcar 807 and Epcar 5465, U.S. Army polymer 2177-14 and a proprietary ARCO polymer, ARCOFLO, of molecular weight reported to be in the range of 15 to 20 million.

Since ARCOFLO, in contrast to Army polymer 2177-14, was soluble in DF 7225 using the cryogenic procedure, a precipitation method was used to determine the concentration. In this case the polymer was precipitated using acetone, washed three times with acetone, dried in vacuum at 40°C for two hours and weighed. The concentration of the stock solution was estimated from the polymer weight and the mass of solution. Concentrations of solutions prepared by dilution of the stock solution were

- 21 -

obtained by multiplying the concentration of the stock solution by the appropriate gravimetric factor, i.e., [mass of stock solution/(mass of stock solution - mass of solvent)] x concentration of polymer in stock solution.

3. RESULTS OF CRYOGENIC GRINDING AND BLENDING OF POLYMER AND DIESEL FUEL

1. Viscometric Calibration Curve

Curves of weight percent polymer in DF "2(?)5 standard fuel (non referee grade was used to establish the practical nature of the cryogenic process after initial tests revealed that cryogenic solvation proceded with equal facility with either standard or referee grade fuel) are shown in Figures 5, 6, 7, 8, 9, 10, 11, and 12, respectively, for solutions of B-100 (BASF), L-180 (Exxon), B-200 (BASF), and B-230 (BASF), Firestone 10955, Natsyn, Gulf AP-11; and Shell SAP-960.

A compilation of available information on these and other polymers evaluated in this project is presented in Table 1. Calibration curve data are summarized in Table 2 using the experimentally determined intrinsic kinematic viscosities and the corresponding concentrations in weight percent. The intrinsic viscosity, $[\eta]$ is $(\eta - \eta_0)/\eta_0$ where η is the viscosity of the solution and η_0 is the viscosity of the solvent. Expressing concentration as a function of $[\eta]$ we obtain the general function

$$C = b[\eta]^a$$

where a and b are constants for each polymer/DF "2(?)5 system. Linear regression data summarized in Table 2 include the number of concentration and intrinsic viscosity data pairs, n, the linear regression coefficient, γ, the slope, a, and the intercept, b from the equivalent linear function.

$$\ln C = a \ln[\gamma] + \ln b.$$

These data can be used to estimate concentrations falling outside of the range of the curves displayed in Figures 5 through 12. It was not necessary to employ this type of extrapolation in this project, however, since gravimetric dilution data were available for all dilutions in the antimisting determinations. Hence, if at least one concentration fell within the concentration range of the calibration curve all other concentrations would be obtained from the gravimetric dilution factors.

FIGURE 5:   B-100 VISCOMETRIC CALIBRATION CURVE OF 7005
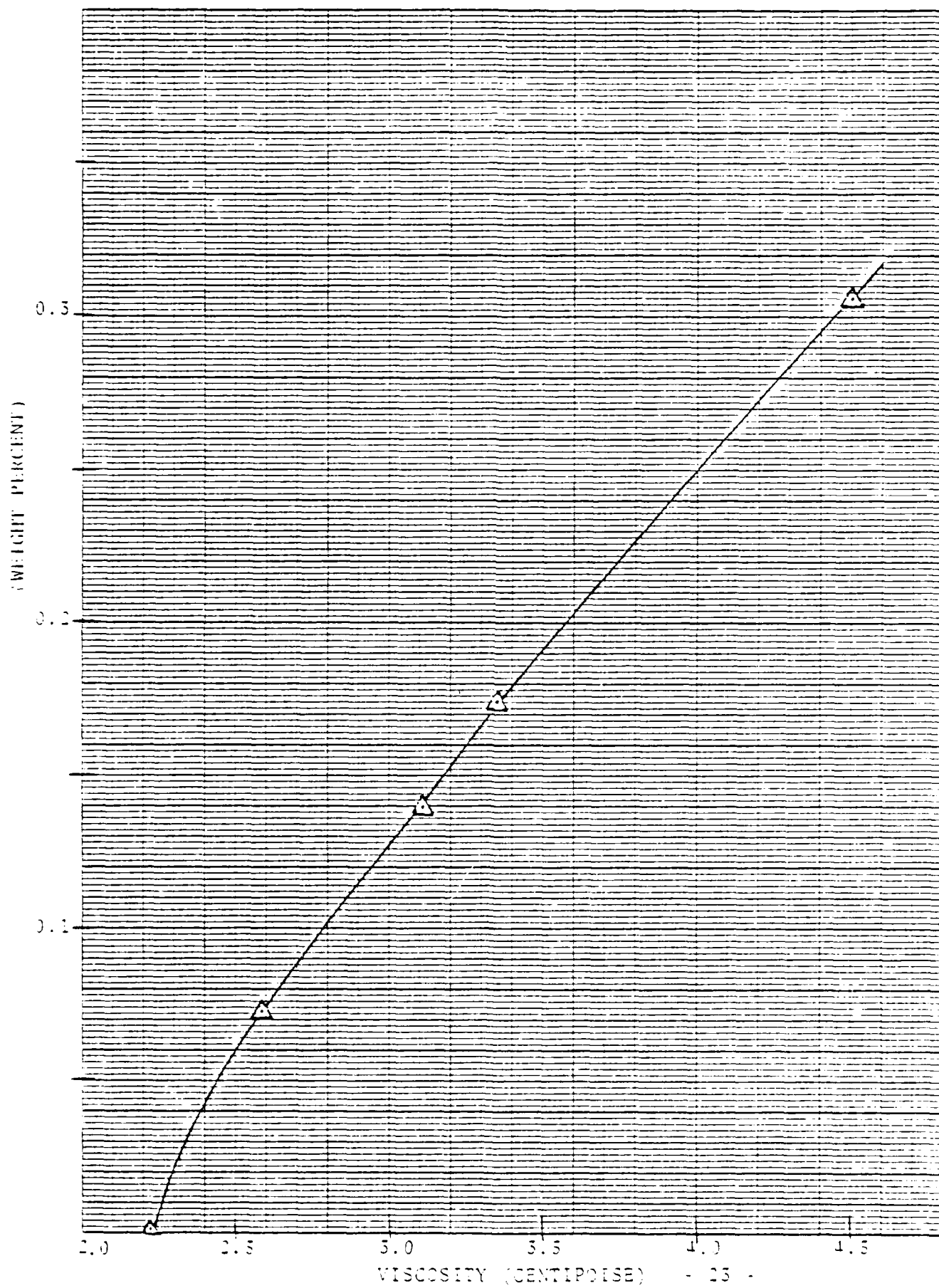
VISCOSITY (CENTIPOISE)   - 23 -

FIGURE 6:   L-130 VISCOMETRIC CALIBRATION CURVE OF 7335

FIGURE 7:   B-100 VISCOMETRIC CALIBRATION CURVE/DF 7035

(WEIGHT PERCENT)

VISCOSITY (CENTIPOISE)
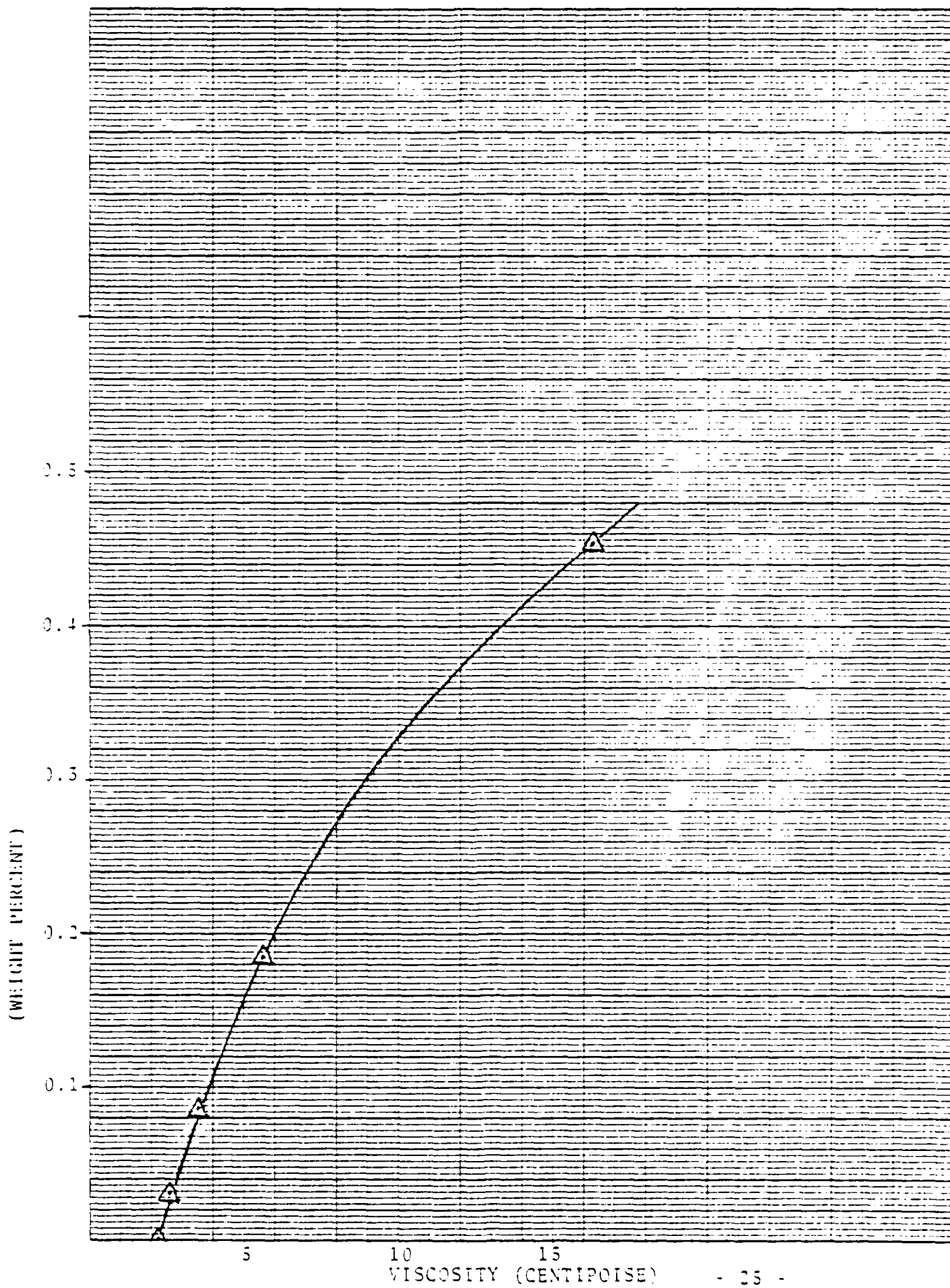
FIGURE 8: B-230 VISCOMETRIC CALIBRATION CURVE OF TDS

(WEIGHT PERCENT)

VISCOSITY (CENTIPOISE) - 26 -
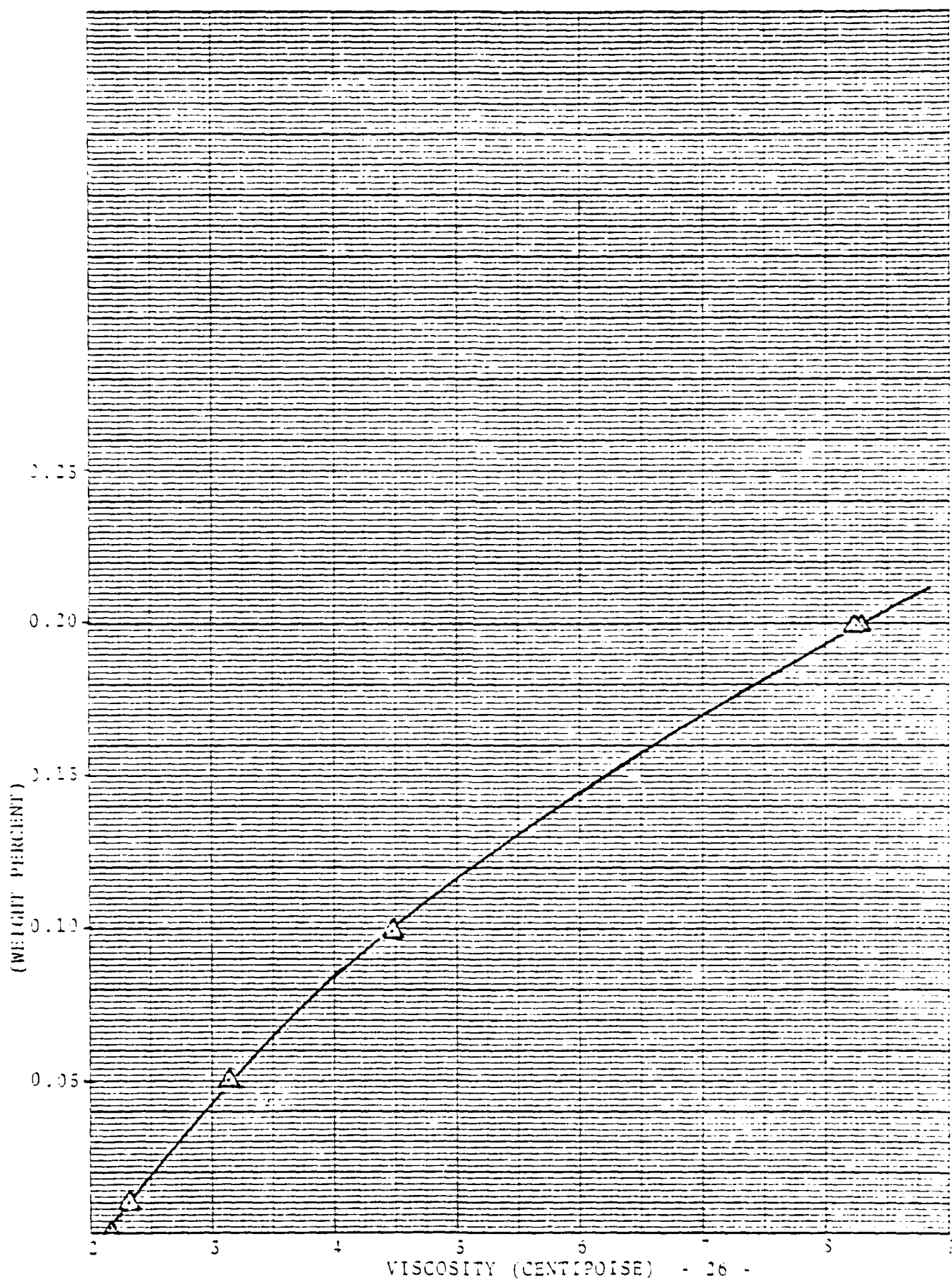
FIGURE 9: FIRESTONE 10955 VISCOMETRIC CALIBRATION CURVE/DF 7225
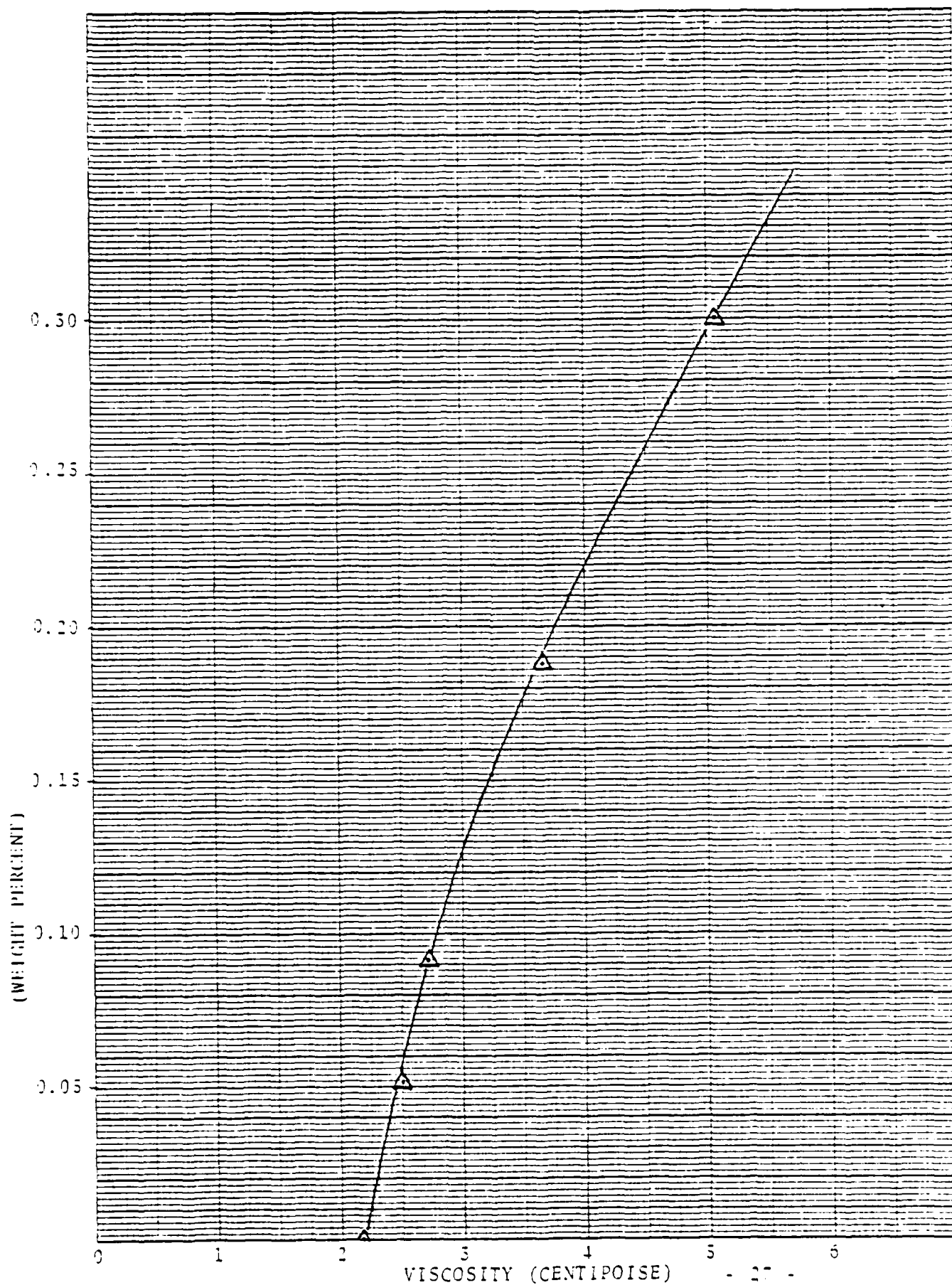
FIGURE 10: NATSYN VISCOMETRIC CALIBRATION CURVE DF 7225

(WEIGHT PERCENT)

VISCOSITY (CENTIPOISE)
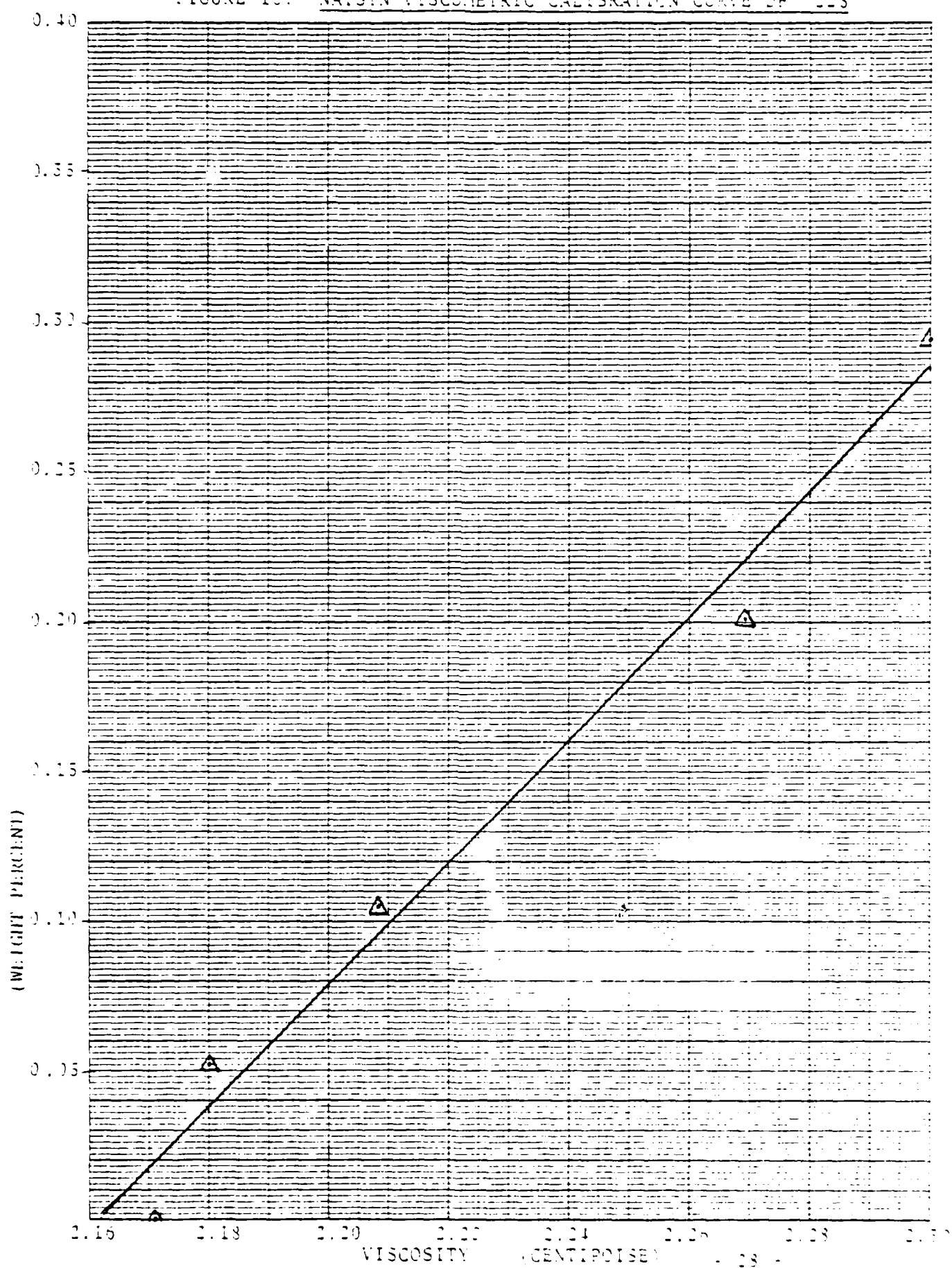
FIGURE 11: GULF AP-11 VISCOMETRIC CALIBRATION CURVE/DF 7005
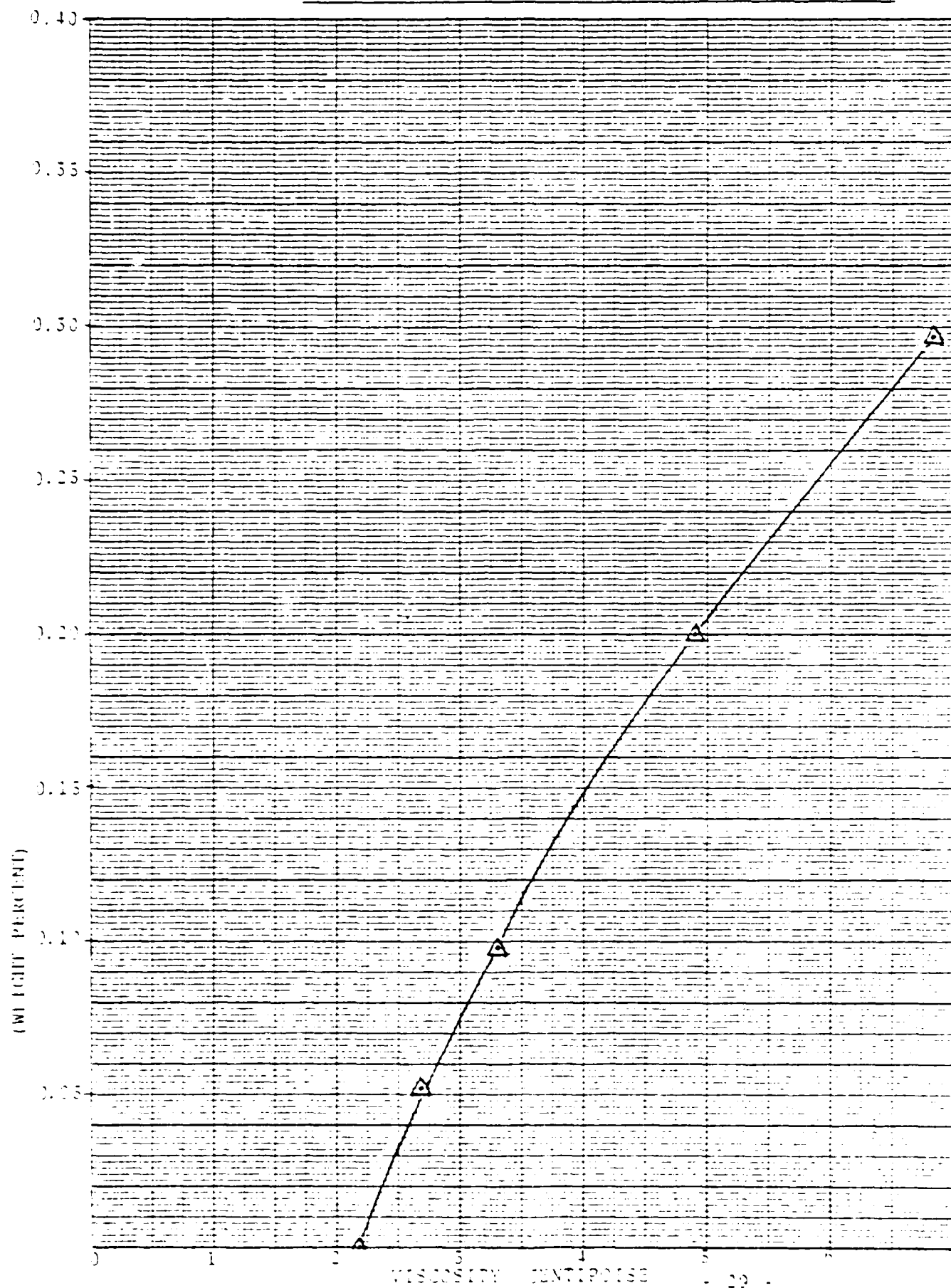
FIGURE 12: SHELL SAP-960 POLYMER VISCOMETRIC CALIBRATION CURVE/DF 7225

VISCOSITY (CENTIPOISE)   - 30 -
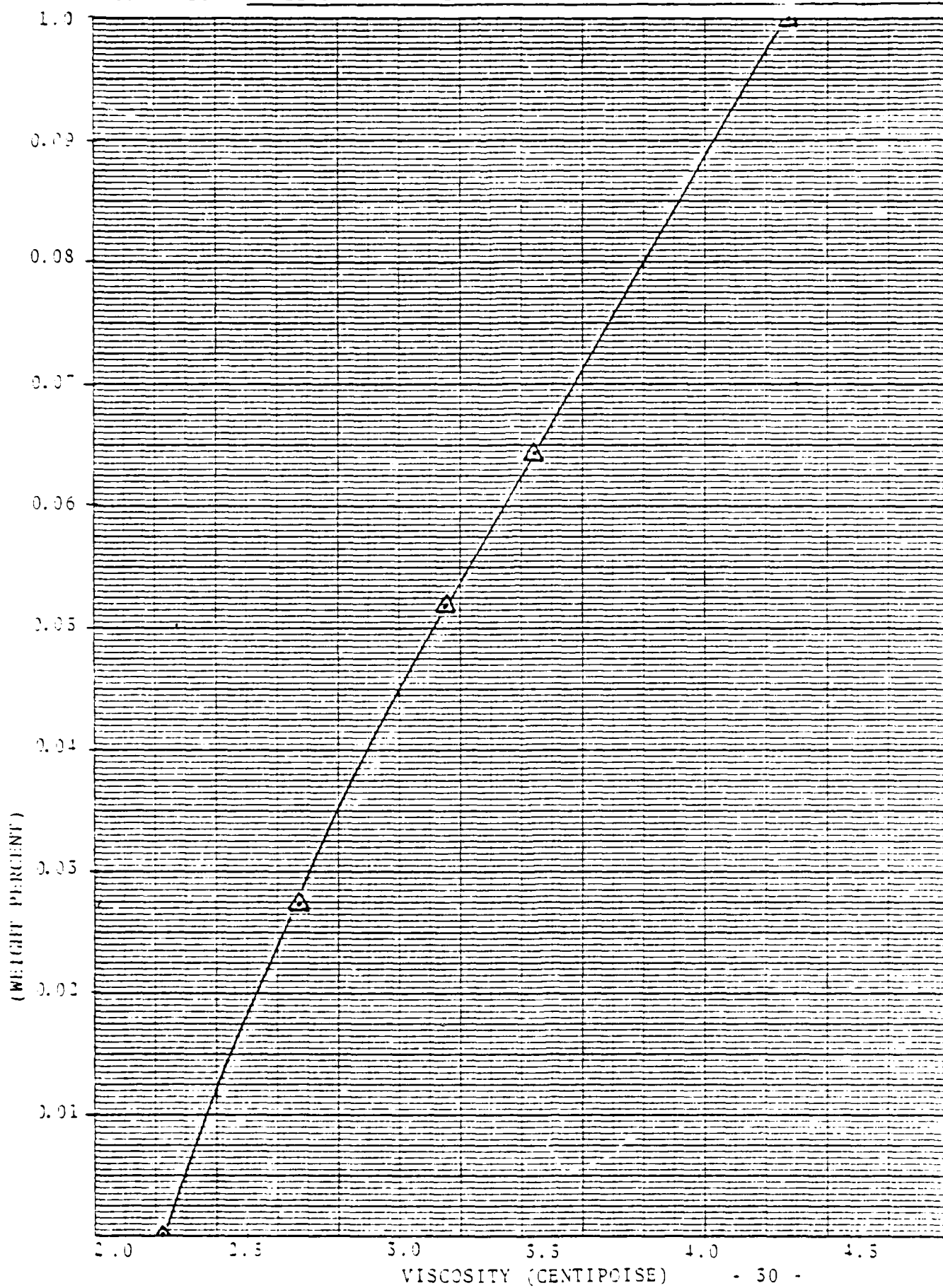
TABLE 1

COMPILATION OF POLYMER DATA AND SUMMARY OF VISCOMETRIC COMMENTS

POLYMER	MANUFACTURER	CHEMICAL NATURE	MOLECULAR WEIGHT	SOURCE	VISCOMETRIC COMMENTS
B-100	BASF	POLYISOBUTYLENE	1.27×10^6	BASF TO GTA	CALIBRATION CURVE FIGURE 5
L-180	EXXON	POLYISOBUTYLENE	3×10^6	ARMY TO GTA	CALIBRATION CURVE FIGURE 6
B-200	BASF	POLYISOBUTYLENE	4.33×10^6	BASF TO GTA	CALIBRATION CURVE FIGURE 7
B-230	BASF	POLYISOBUTYLENE	5.6×10^6	BASF TO GTA	CALIBRATION CURVE FIGURE 8
10955	FIRESTONE	POLYBUTADIENE	1.2×10^6	ARMY TO GTA	CALIBRATION CURVE FIGURE 9
NATSYN	GOODYEAR	POLYISOPRENE	1×10^6	ARMY TO GTA	CALIBRATION CURVE FIGURE 10
EPCAR 5465	GOODRICH	SATURATED HYDROCARBON	4×10^5	ARMY TO GTA	STOCK SOLUTION COULD NOT BE PREPARED CONVEN
EPCAR 807	GOODRICH	HYDROCARBON WITH SOME UNSATURATION	2×10^5	ARMY TO GTA	STOCK SOLUTION COULD NOT BE PREPARED CONVEN
2177-14	U.S. ARMY	POLYARYLOXYPHOS-PHAZINE	NOT AVAILABLE	ARMY TO GTA	STOCK SOLUTION COULD NOT BE PREPARED CONVEN
AP-11	GULF	PROPRIETARY	$15-20 \times 10^6$	GULF TO GTA	CALIBRATION CURVE FIGURE 11
SAP-960	SHELL	PROPRIETARY	NOT AVAILABLE	SHELL TO GTA	CALIBRATION CURVE FIGURE 12
ARCOFLO	ARCO	PROPRIETARY	NOT AVAILABLE	ARCO TO GTA	STOCK SOLUTION COULD NOT BE PREPARED CONVEN

TABLE 2

LINEAR REGRESSION ANALYSIS OF CALIBRATION CURVE

where $C = b[\eta]^a$ or $\ln C = a \ln [\eta] + \ln b$

POLYMER	NUMBER OF DATA SETS (n)	LINEAR REGRESSION COEFFICIENT (γ)	SLOPE (a)	INTERCEPT (b)
B-100	5	0.9995	1.093	0.3787
L-130	5	0.9996	1.038	0.1769
B-200	8	0.9816	1.036	0.1865
B-230	5	0.9920	0.9917	0.09791
10955	5	0.9991	1.073	0.3136
NATSYN	5	0.9913	1.377	25.47
AP-11	5	0.9994	1.036	0.1737
SAP-960	5	0.9999	1.013	0.1210

2.   Immediate Antimisting Effectiveness of Freshly
      Prepared Solutions

      A summary of antimisting behavior of cold polymer solu-
tions in DF 7225 is presented with comments in Table 5. These
solutions were passed through the sprayer immediately after com-
pleting the cryogenic grinding/fuel blending operation as described
previously in the experimental section under the Spex Analytical
Hammer-Cutter Mill. These initial qualitative observations were
then followed by measurement of the antimisting ratio as a func-
tion of polymer concentration as described in the previous section
on the antimisting fuel effectiveness tester. Gravimetric dilution
data and corresponding solution viscosities were obtained during
antimisting effectiveness testing.

      As mentioned previously, the solution process was inde-
pendent of whether standard lot or referee grade DF 7225 was used.
Grinding requirements were sensitive to the nature of the polymer,
and some polymers, for example the very tacky ARCOFLO, were diffi-
cult to keep cold enough for effective cryogrinding, especially in
long runs with high likelihood of impact heating. This deficiency
in grinder design and heat transfer at cryogenic temperatures is
less severe in the Bantam Mill.

      Antimisting behavior was seen, as shown in Table 5, very
soon after completion of the cryogenic grinding/fuel blending in
the case of all the polymers which also formed solutions by the
lengthy conventional method. The single exception was ARCOFLO,
which was put into solution rapidly by the cryogenic process, but
would not go into solution completely by the conventional approach.
Although subsequent quantitative analysis of antimisting behavior
revealed that the Epcar polymers were placed in solution through
the cryogenic process, the level of antimisting relative to other
polymers tested was very slight. Further study of the Epcar poly-
mers was not pursued.

      Study of the time-course of antimisting behavior and of
the viscosity is confounded by the fact that freshly prepared
solutions are very cold, often in the range of -10° to 10°C in a
successful run. In an unsuccessful run where the fuel flow rate
is too low or the liquid nitrogen flow rate is too high, the fuel
can freeze. Short of freezing, however, low temperature did not
destroy the antimisting effectiveness of the solutions in Table 2.
Data were not developed to show antimisting effectiveness as a
function of fuel temperature.

3.   Comparative Analysis of Antimisting Effectiveness

      A fire resistance test is the preferred method to use
in testing polymer additives for enhancing the fire resistance

TABLE 3

ANTIMISTING BEHAVIOR OF POLYMER SOLUTIONS IN DF 7225 IMMEDIATELY AFTER CRYOGENIC GRINDING AND FUEL BLENDING

POLYMER	CONCENTRATIONS IN WEIGHT PERCENT (1)	TIME FROM GRINDING TO TESTING (MIN)	TEMPERATURE (C°) OF SOLVATION AT TIME OF TESTING	ANTIMISTING BEHAVIOR RELATIVE TO B 2301
NATSYN	1.068	10	5-9	MODEST
EPCAR 5465	--	12	10	VERY SLIGHT
10955	--	7	10	VERY SLIGHT
10955 REPEAT	0.019	8	11	VERY SLIGHT
EPCAR 807	--	5	10	VERY SLIGHT
2177-14	INSOLUBLE	7	--	NONE
AP-11	0.055	15	8	MODEST
ARCOFLO	0.5118	12	--	VERY GOOD
ARCOFLO REPEAT	--	8	16	VERY GOOD
SAP-960	0.016	4	10	APPEARS TO BE SLIGHT (2)
SAP-960	--	18	10	APPEARS TO BE SLIGHT

TABLE 3 (CONTINUED)

POLYMER	CONCENTRATIONS IN WEIGHT PERCENT (1)	TIME FROM GRINDING TO TESTING (MIN)	TEMPERATURE (°C) OF SOLVATION AT TIME OF TESTING	ANTIMISTING BEHAVIOR (RELATIVE TO B-230)
EPCAR 807		--	--	NONE, IMMEDIATELY AND NONE AFTER 20 MINUTES
B-100	0.118	--	--	VERY GOOD
L-180	0.092	--	--	VERY GOOD
B-200	0.150	--	--	EXCELLENT
B-230	1.075	--	--	OUTSTANDING (3)

(1) Determined during development of quantitative antimisting vs concentration plots.

(2) Subsequent quantitative analysis of antimisting behavior revealed substantial anti misting effectiveness obscured to the eye because viscoelastic strands are not obvious. This polymer may impart antimisting character through a different mechanism than that typical of high molecular weight polyisobutylene solutions in DF 7225.

(3) Concentration of stock solution was much higher than those of the other polymer solutions. Subsequent quantitative analysis of antimisting behavior revealed that, on an equal concentration basis, B-230 was the most effective polymer in the test series.

of diesel fuel. The present project, however, serves as a means of determining the suitability of using the cryogenic grinding solution process by rapidly preparing diesel fuel blends containing polymeric additives.

Since a large number of polymer candidates were investigated, it was necessary to develop a quantitative test for characterizing the antimisting effectiveness of solutions in diesel fuel. Although the test does not measure fire resistance, it does provide data on the mist generation, under the same conditions, associated with each polymer solution. By plotting antimisting effectiveness against polymer concentrations, enough data is obtained to compare different polymers and to then select the most promising candidates for fire resistance and engine performance testing.

The gravimetric antimisting effectiveness test apparatus and methodology has been described previously in this experimental section.

Antimisting vs concentration data are presented in three formats in this section. Graphs of $-\ln\left(\frac{P-R}{P}\right)$ (relative antimisting index) vs concentration are presented in Figures 13 through 21. The data points on these graphs are presented in Table 4. The linear regression data for the lines in Figures 13 through 21 are displayed in Table 5. Both Table 5 and Table 6 can be used to facilitate comparative analysis of the antimisting effectiveness of the different polymer candidates.

After discussing the data in Table 6 with the project officer, the most promising candidates for the production of 5 gallon samples for fire resistance and engine performance testing were determined to be B-250, ARCOFLO and Shell SAP-960. Although the Gulf polymer showed an antimisting effectiveness equal to that of B-200, it is our understanding that it is only the first attempt to develop a tailored fire resistance polymer additive for use in JET A for aviation turbines. The decision was made to await further development of this polymer system in the development program of the Federal Aviation Administration.

The data presented in Tables 4, 5 and 6 will be discussed under Discussion of Results.

4. **The Influence of Polymer Molecular Weight on Antimisting Effectiveness**

In order to investigate the role of molecular weight on antimisting effectiveness it was necessary to use a well characterized polymer available in a range of molecular weights. One polymer from Exxon, L-180, and three from BASF, B-100, B-200 and

FIGURE 13: B-100 ANTIMISTING VS POLYMER CONCENTRATION
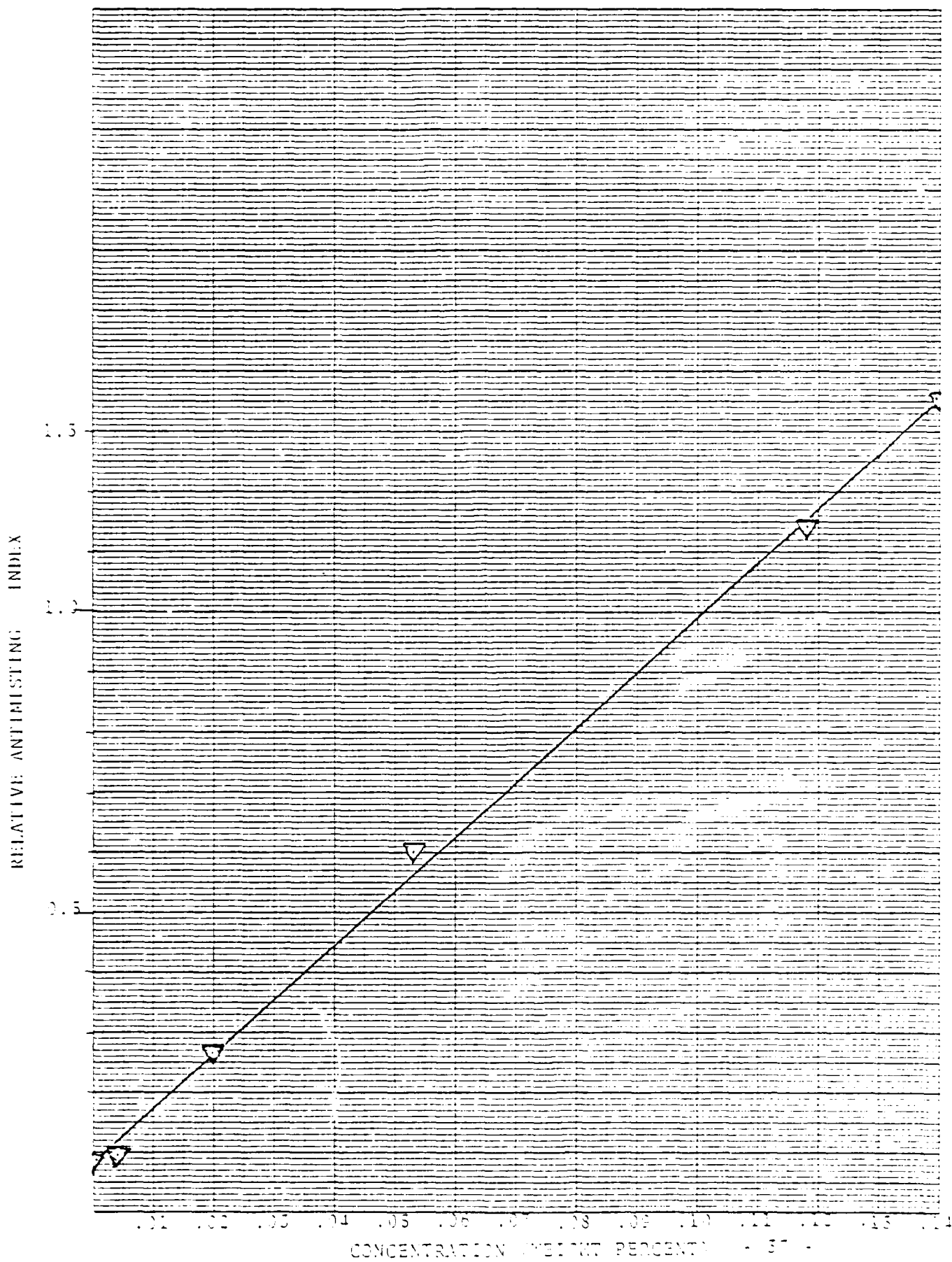
CONCENTRATION WEIGHT PERCENT   - 37 -

FIGURE 14: L-180 ANTIMISTING VS POLYMER CONCENTRATION

RELATIVE ANTIMISTING INDEX

CONCENTRATION (WEIGHT PERCENT) - 33 -

FIGURE 15: B-200 ANTIMISTING VS POLYMER CONCENTRATION

RELATIVE ANTIMISTING INDEX

CONCENTRATION (WEIGHT PERCENT)
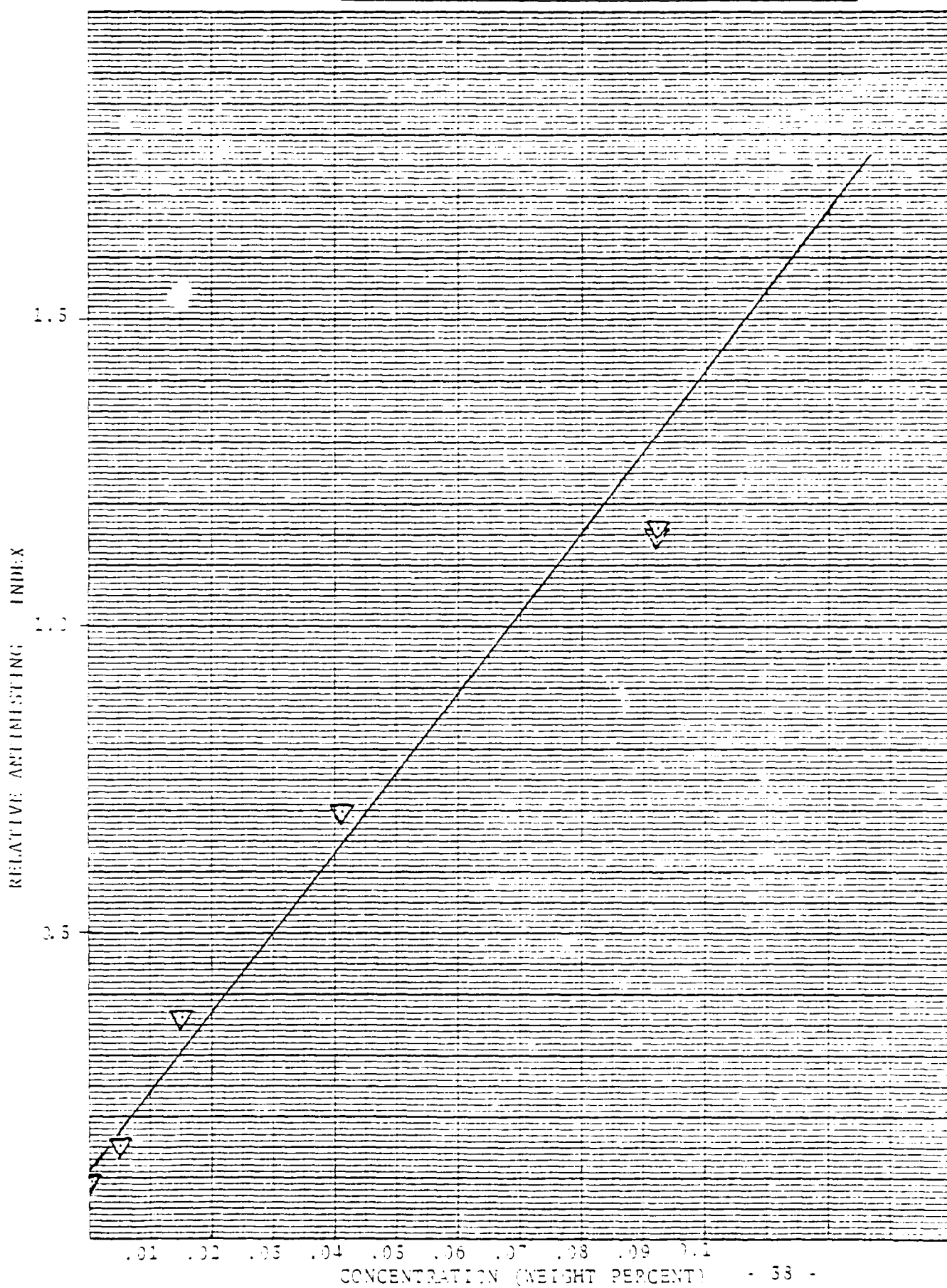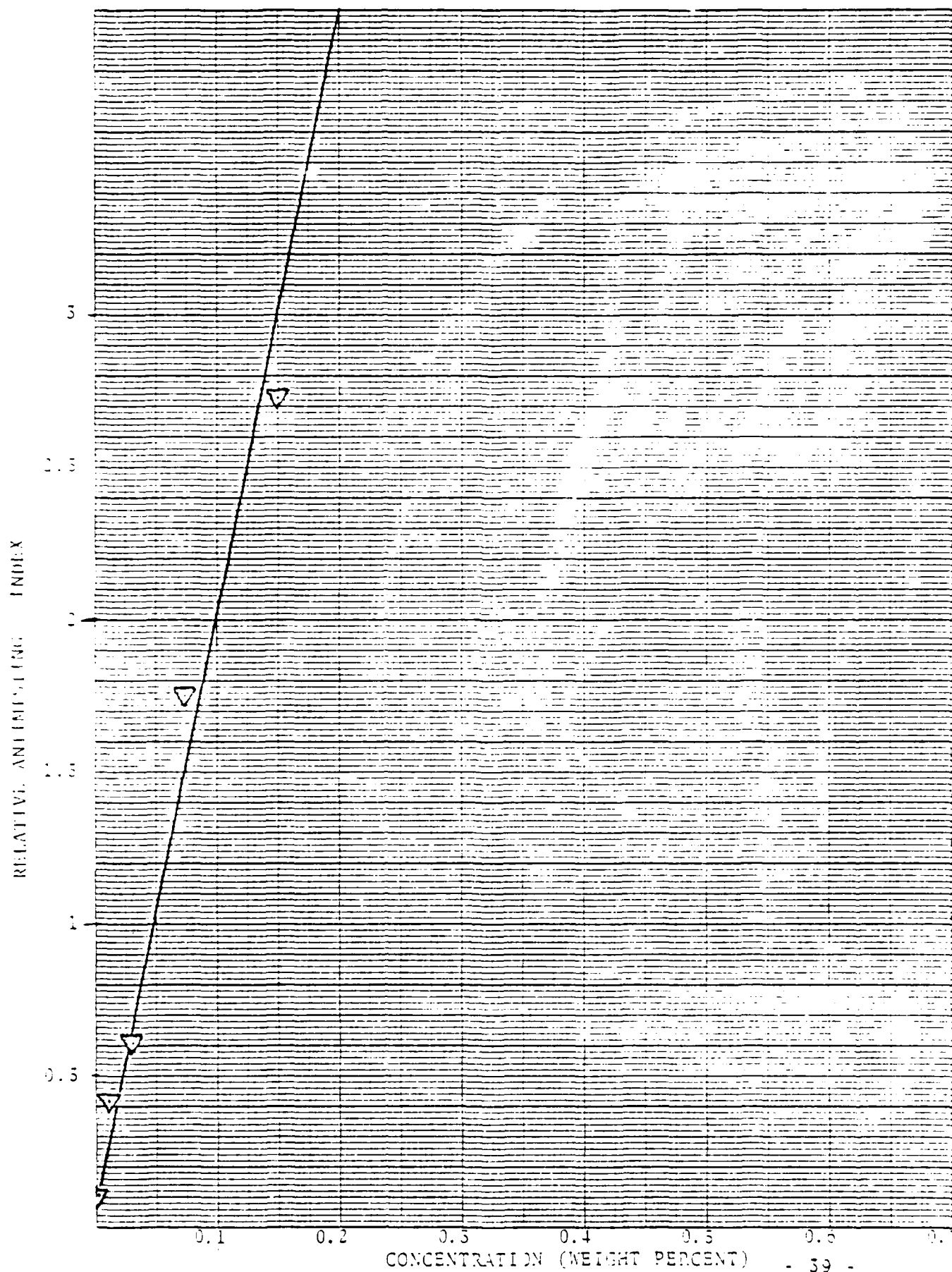
FIGURE 16:   B-230 ANTIMISTING VS POLYMER CONCENTRATION

CONCENTRATION (WEIGHT PERCENT)   - 40 -
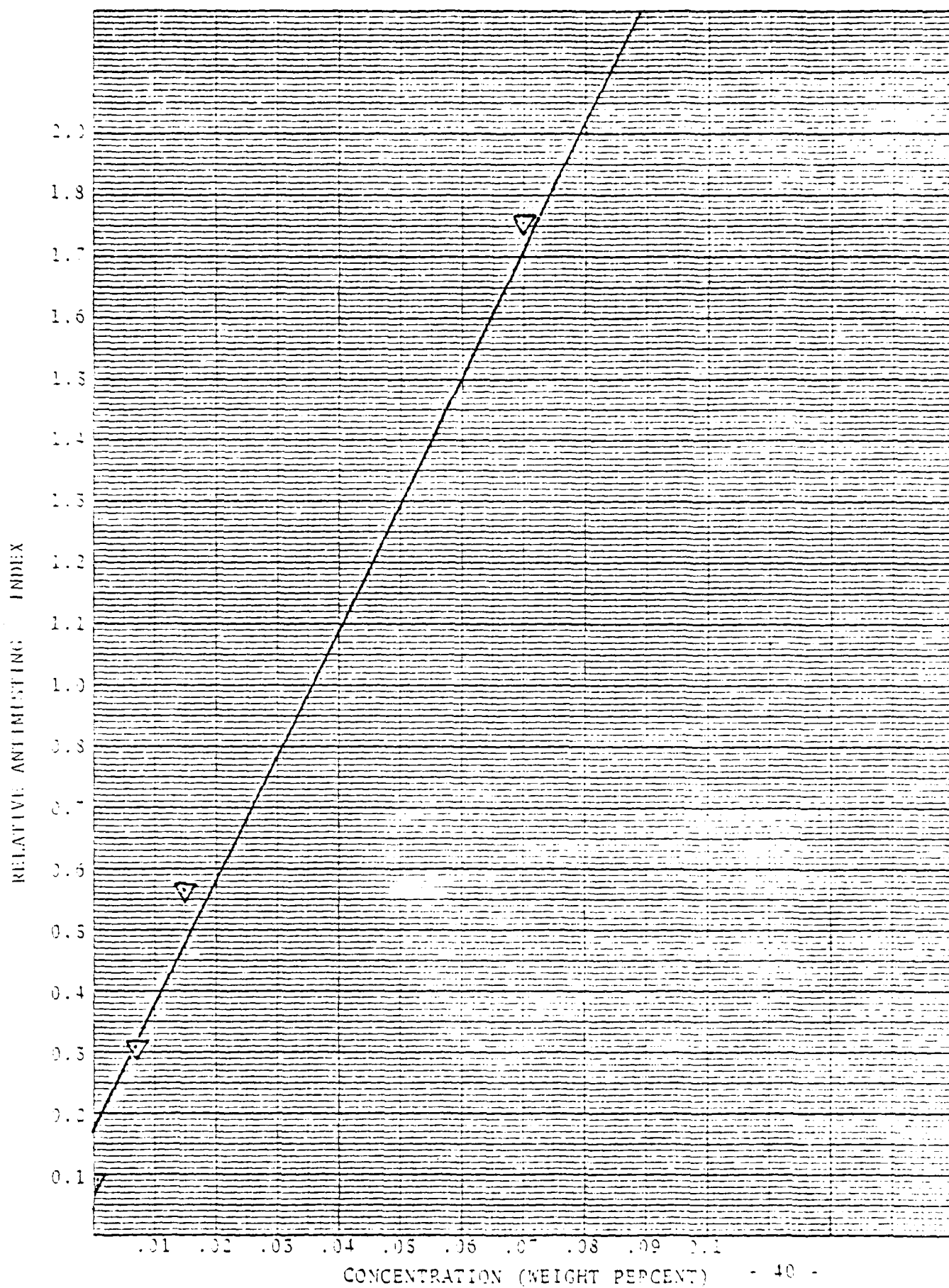
FIGURE 17: FIRESTONE RDP 1-055 ANTIMISTING AS POLYMER CONCENTRATION

CONCENTRATION (WEIGHT PERCENT) - 41 -
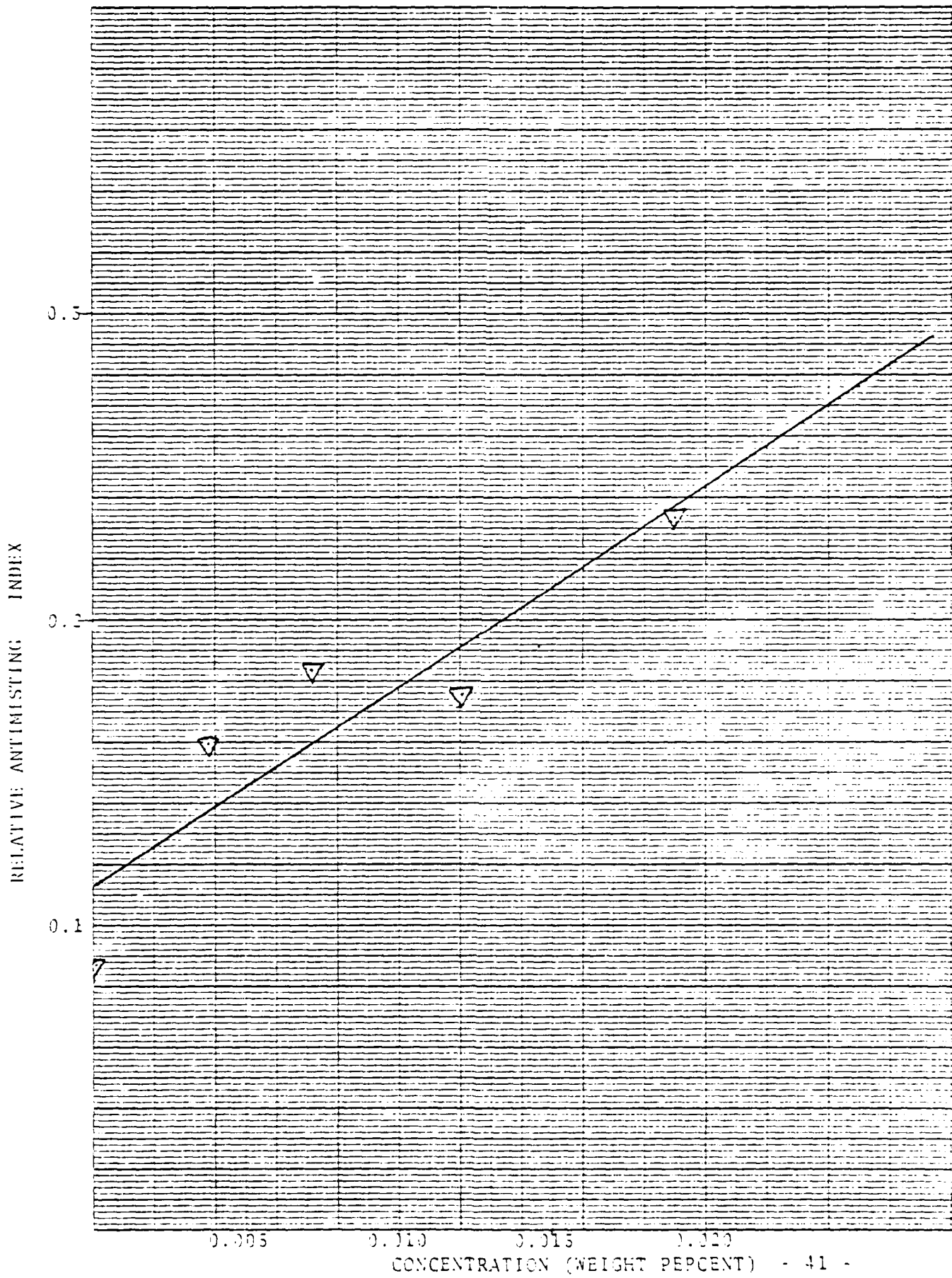
FIGURE 18: NATSYN ANTIMISTING VS POLYMER CONCENTRATION

RELATIVE ANTIMISTING INDEX

CONCENTRATION (WEIGHT PERCENT)

- 46 -
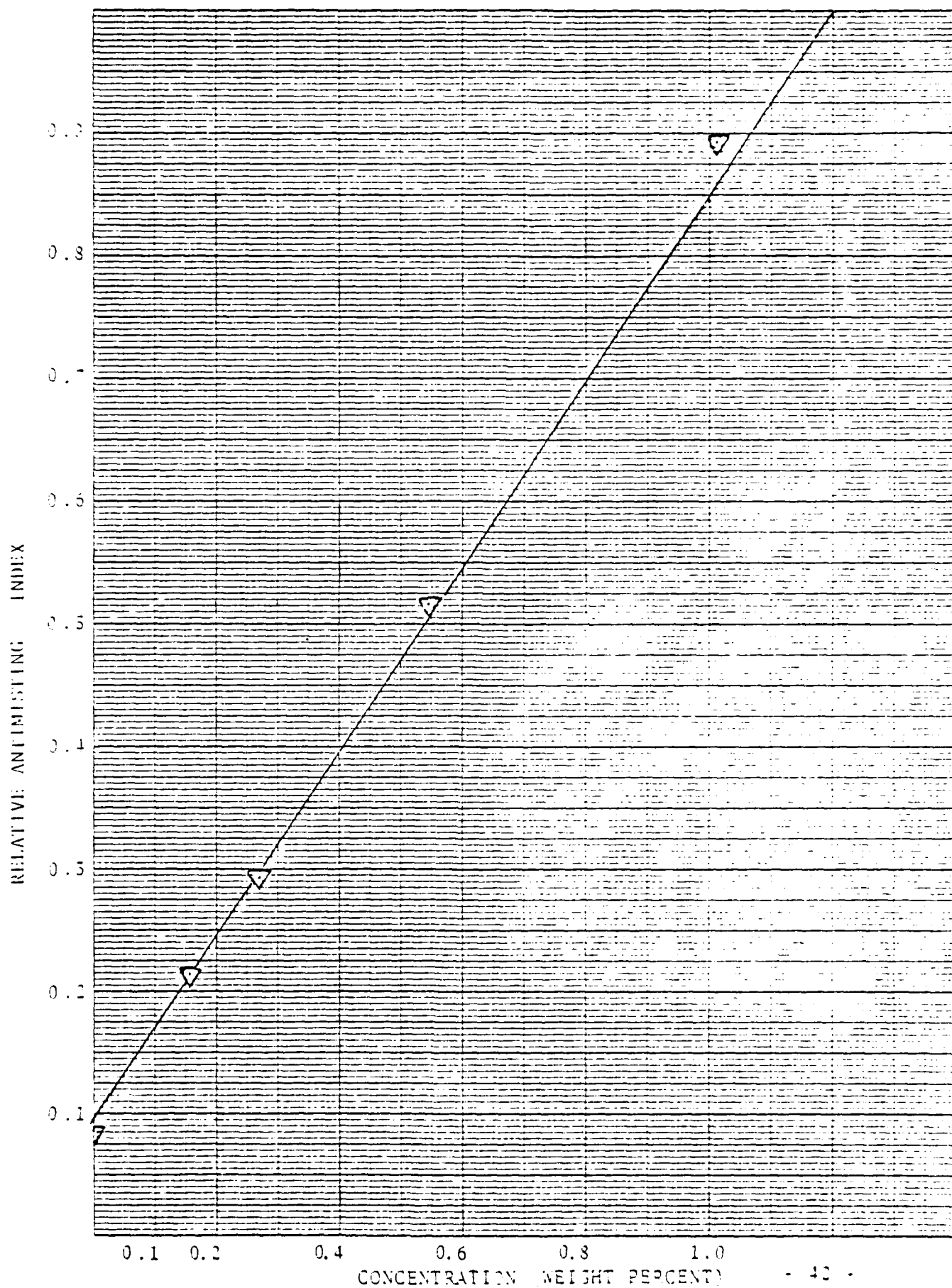
FIGURE 19: GULF AP11 ANTIMISTING VS POLYMER CONCENTRATION
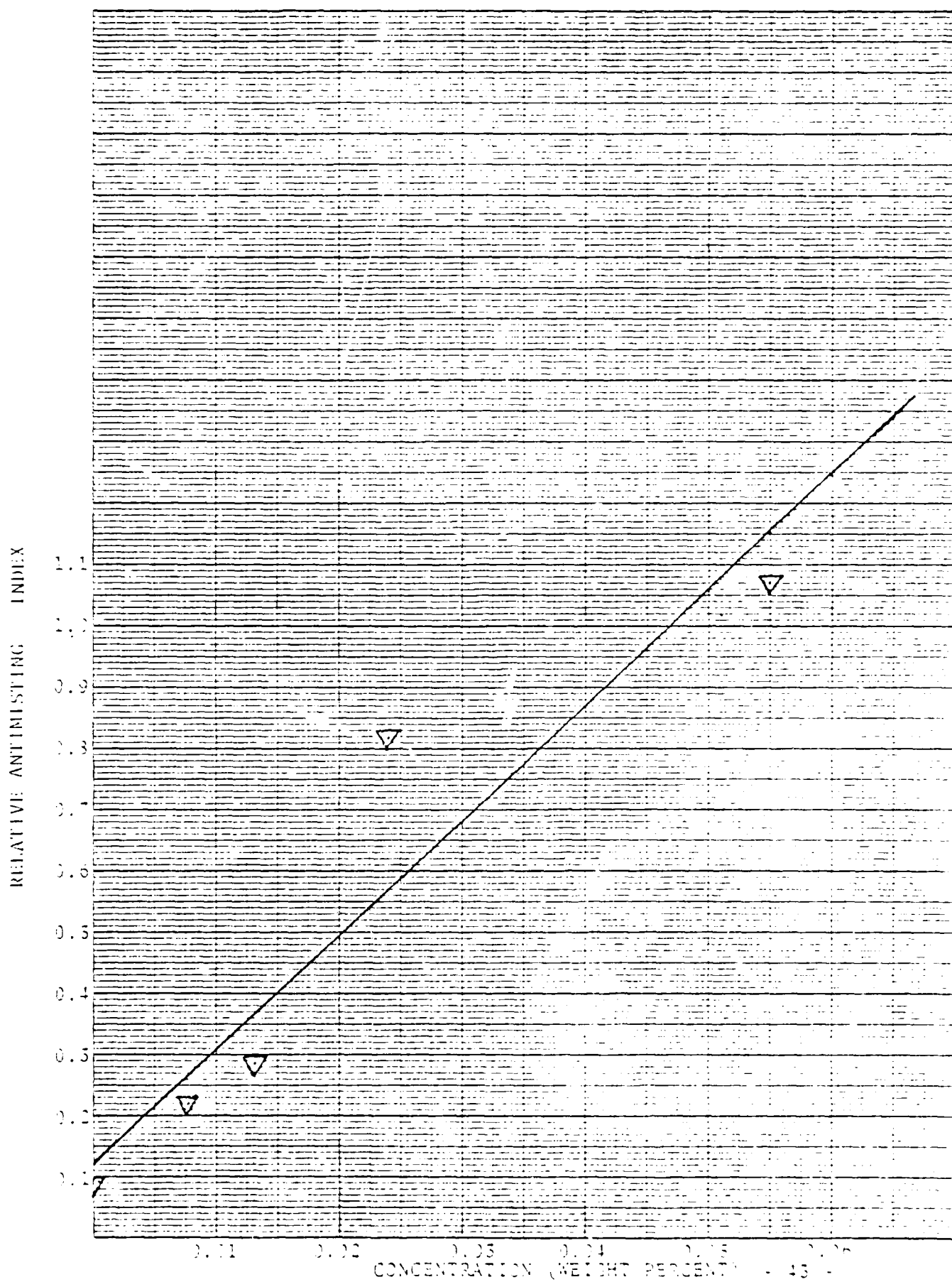
FIGURE 20:   SHELL SAP-960 ANTIMISTING VS POLYMER CONCENTRATION

RELATIVE ANTIMISING   INDEX

CONCENTRATION (WEIGHT PERCENT)   - 44 -
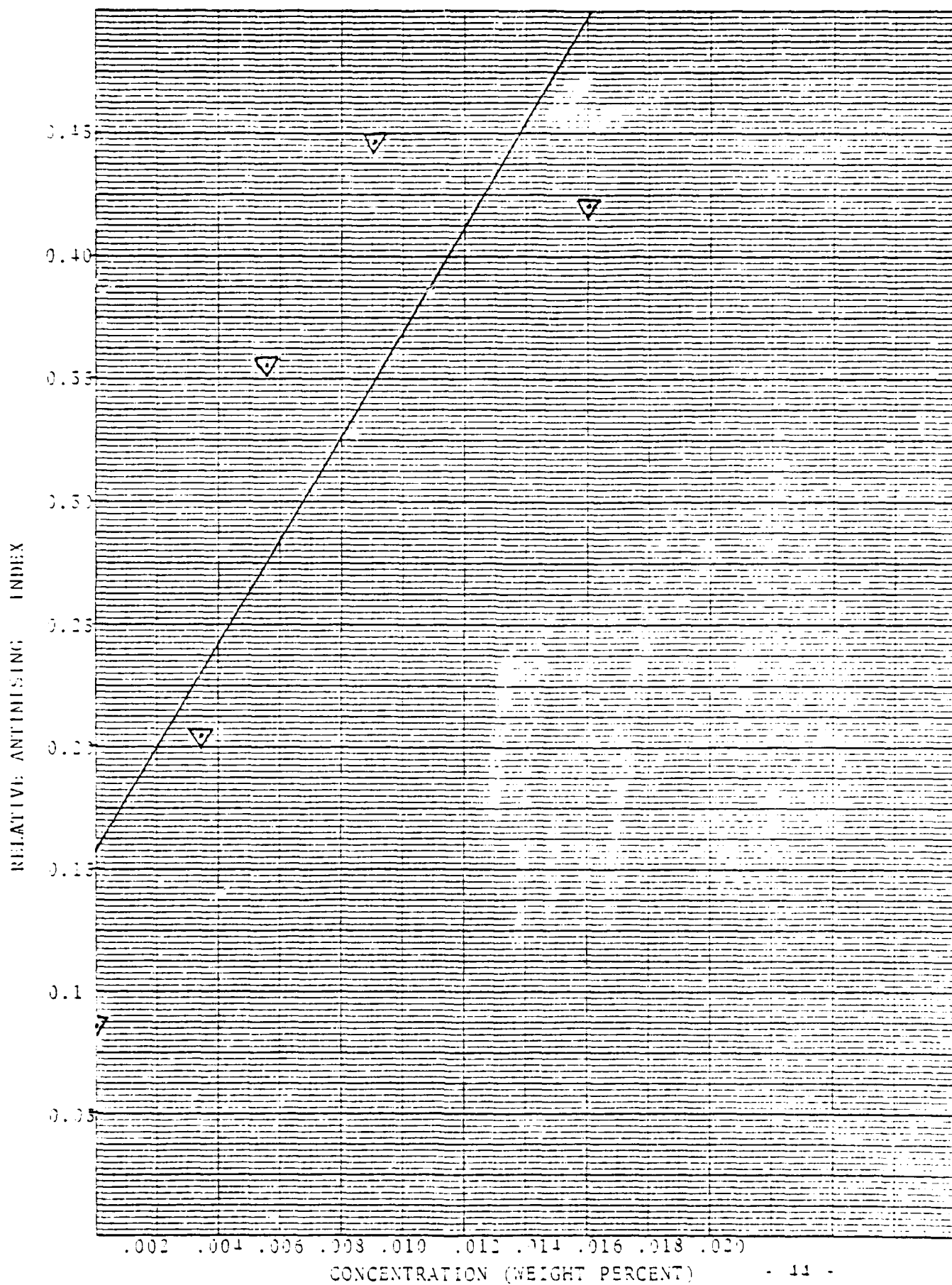
FIGURE 21:   ARCOFLOW ANTIMISTING VS POLYMER CONCENTRATION

- 45 -
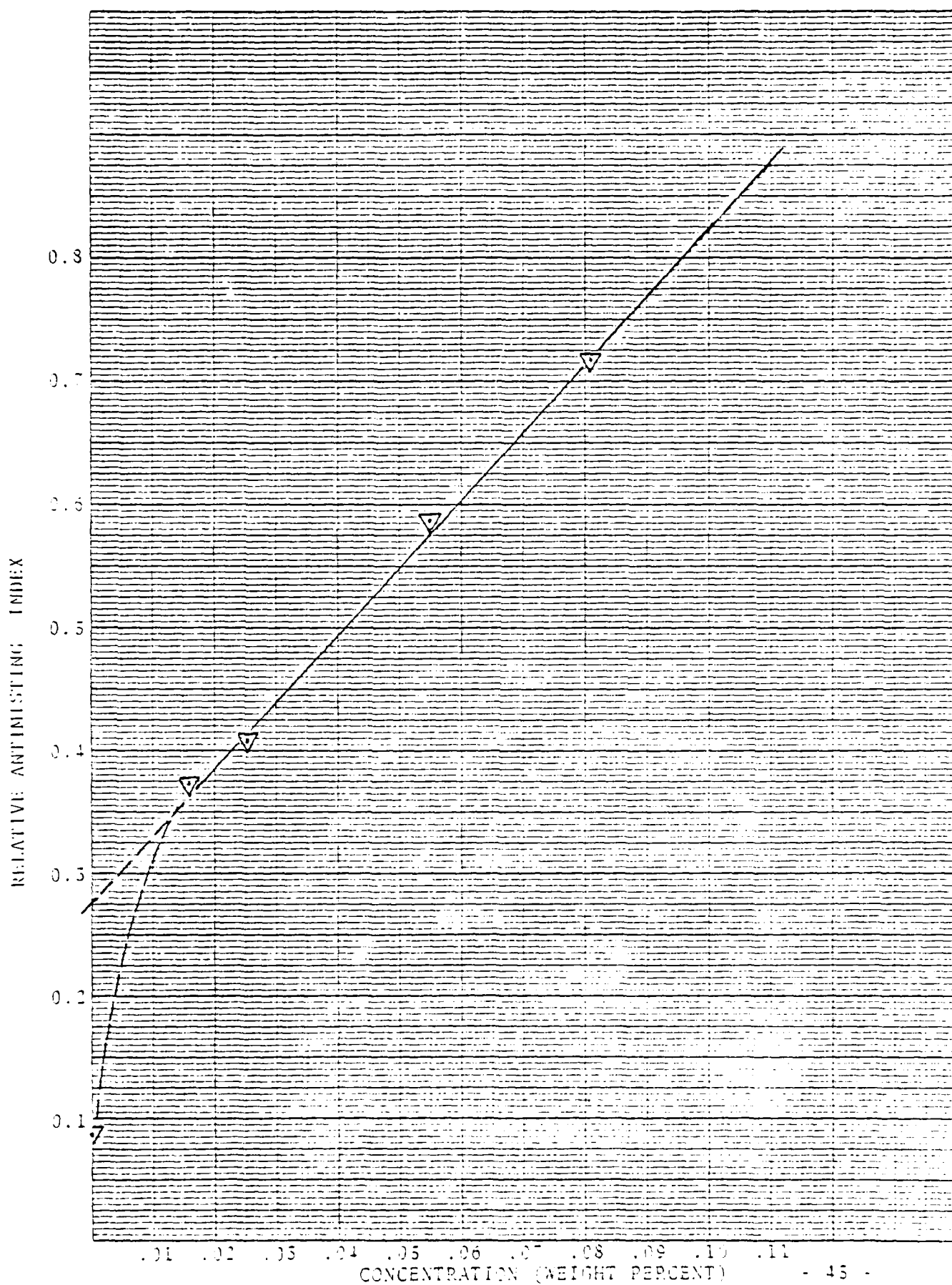
TABLE 4

RELATIVE ANTIMISTING INDEX VS CONCENTRATION OF POLYMER SOLUTIONS IN ⁊025 DIESEL FUEL

B-100

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	(CENTIPOISE)	CONCENTRATION WT % FROM ⁊	GRAVIMETRIC
1	1.0	1.1389	2.93	0.118	0.118
2	0.4520	0.6003	2.54	0.067	0.0533
3	0.1707	0.2600	2.39	0.043	0.0201
4	0.02958	0.09477	2.33	0.037	0.0035
FUEL	0.0	0.08612	2.30	-	-

L-180

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	(CENTIPOISE)	CONCENTRATION WT % FROM ⁊	GRAVIMETRIC
1	1.0	1.3054	3.17	0.092	0.092
1	1.0	1.2905	3.17	0.092	0.092
2	0.4407	0.6951	2.62	0.043	0.041
3	0.1627	0.3566	2.54	0.015	0.015
4	0.04925	0.1467	2.25	0.006	0.005

B-200

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	(CENTIPOISE)	CONCENTRATION WT % FROM ⁊	GRAVIMETRIC
1	1.0	2.731	4.80	0.150	0.150
2	0.4847	1.751	3.24	0.072	0.073
3	0.1998	0.6019	2.59	0.03	0.03
4	0.07758	0.4072	2.35	0.012	0.012

* Ratio of the mass of solution of concentration x to the mass of solution of concentration x plus added solvent.

TABLE 4

TABLE 4 (CONTINUED)

B-250

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	(CENTIPOISE)	CONCENTRATION ... FROM ?	GRAVIMETRIC
1	1.0	Not pumpable	390.0	-	1.0746
2	0.4436	Not pumpable	Not measured		0.4767
3	0.1742	Not pumpable	33.5		0.1872
4	0.06515	1.753	3.63	0.070	0.070
5	0.01555	0.5612	2.47	0.0175	0.015
6	0.006544	0.5013	2.33	0.010	0.00705
FIRESTONE ADP 10955					
1	1.0	0.2330	2.27	0.019	0.019
2	0.6107	0.1749	2.25	0.015	0.012
3	0.3781	0.1829	2.23	0.010	0.0072
4	0.1980	0.1585	2.23	0.010	0.0055
NATSYN					
1	1.0	0.8924	2.68	1.063	1.063
2	0.5148	0.5143	2.44	0.5725	0.5498
3	0.2559	0.2933	2.33	0.3456	0.2733
4	0.1498	0.2149	2.29	0.2631	0.1600

* Ratio of the mass of solution of concentration x to the mass of solution of concentration x plus added solvent.

TABLE 4 (CONTINUED)

EPCAR 5465

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	η (CENTIPOISE)	CONCENTRATION WT. % FROM η	GRAVIMETRIC
1	1.0	0.5006	2.45	No Calib. Curve	
2	0.5561	0.2141	2.33		
3	1.0	0.4821	2.44		
4	0.4596	0.2107	2.51		
5	0.1780	0.1353	2.25		

EPCAR 807

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	η (CENTIPOISE)	CONCENTRATION WT. % FROM η	GRAVIMETRIC
1	1.0	0.1253	2.25		
2	0.6059	0.1329	2.25		

GULF AP-11

NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	η (CENTIPOISE)	CONCENTRATION WT. % FROM η	GRAVIMETRIC
1	1.0	1.070	2.74	0.055	0.055
2	0.4342	0.8141	2.45	0.024	0.024
3	0.2415	0.2844	2.52	0.016	0.015
4	0.1575	0.2191	2.27	0.011	0.0076
FUEL	0.0	Not Measured	2.21	0.000	0.000

*Ratio of the mass of solution of concentration x to the mass of solution of concentration x plus added solvent.

TABLE 4 (CONTINUED)

ARCOFLO NUMBER	CONCENTRATION FACTOR *	ANTIMISTING	η (CENTIPOISE)	CONCENTRATION WT. % FROM η	GRAVIMETRIC
1	1.0	0.7171	3.41		**0.0407 - 0.0813
2	0.6786	0.5835	2.98		0.0275 - 0.05517
3	0.3136	0.4070	2.54		0.01275 - 0.02550
4	0.2010	0.3724	2.43		0.00817 - 0.01634
SHELL SAP-960					
1	1.0	0.4217	2.48	0.016	0.0160
2	0.5705	0.4474	2.39	0.0105	0.00913
3	0.3482	0.3558	2.35	0.0080	0.00557
4	0.2170	0.2049	2.35	0.0065	0.00347

* Ratio of the mass of solution of concentration x to the mass of solution of concentration x plus added solvent.

** Uncertainty in concentration; see footnote Table 5.

TABLE 5

LINEAR REGRESSION DATA FOR ANTIMISTING,
$-\ln(\frac{P-R}{P})$, VS CONCENTRATION IN WEIGHT
PERCENT. SOLVENT OF 225.

POLYMER	CORRELATION COEFFICIENT (γ)	SLOPE (m)	INTERCEPT (b)
B-100	0.9989	9.074	0.08232
L-130	0.9975	13.03	0.1122
B-200	0.9876	17.86	0.1722
B-250	0.9975	23.25	0.1404
RDP 10955	0.0901	6.534	0.1122
NATSYN	0.9998	0.7545	0.09068
AP-11	0.9461	13.698	0.1223
SAP-960	0.8442	21.25	0.1579
ARCOFLO*	0.9988		0.2781

*See graph (Figure 21). This polymer exhibits a break in the
linearity of $-\ln(\frac{P-R}{P})$ vs C in the low concentration region, i.e.,
below 75-150 ppm. The data in the table pertain to the concen-
tration range of 75-150 to 400-800 ppm. The slope in the 0 to
75-150 ppm range is estimated to be approximately a factor of
two greater than that shown in Table 5. There is great uncertainty
in the concentration. The polymer, after precipitation and washing
was dried at low temperature for only 2 hours in a vacuum oven.
Since the polymer was of unknown chemical nature, care was exer-
cised to prevent "unzipping." Assuming 50% of the polymer sample
weight was fuel, m is 10.87.

B-130 were selected. All of these polymers are polyisobutylenes with good thermodynamic compatibility with JP [?].

When C_{53} mist (previously defined as $(2.336-b)/m$) is plotted against the molecular weight of the polymer, the smooth function shown in Figure 22 is obtained. A good fit ($N = 0.9999$) is obtained from the exponential function

$$C_{53} = 4,290e^{-(2.254 \times 10^{-7})MW}$$

where MW is the viscosity average molecular weight. The form of this equation is consistant with the idea that the elongational, or Trouton viscosity is involved in antimisting effectiveness. In this concept the elongational viscosity is proportional to $e^{\tau\dot{\epsilon}}$ where τ is the relaxation time and $\dot{\epsilon}$ is the rate of elongation per unit length (time $^{-1}$). Since τ increases with increasing molecular weight, the good fit of the equation to the data is not unexpected. This will be discussed again in the next section which is organized according to the objectives of this project.

C. DISCUSSION OF RESULTS

### 1. Cryogenic Blending of Polymer Candidates in Fuel

Although the small mill and blending system was inferior in basic design to the larger mill used to prepare 5 gallon samples, it was used successfully to prepare small quantities of polymer solutions for investigation.

Cryogenic blending using the small mill system was successfully applied to all of the polymers listed in Table 1 except U.S. Army polymer 2177-14. In the other cases, antimisting behavior was seen in the cold solutions immediately after grinding and blending. All of these solutions were characterized for antimisting effectiveness.

The Bantam mill design is closer to the optimum for preparing polymer solutions than the Spex design. The Spex mill size, however, facilitates the preparation of small samples and can be quickly cleaned and reused with a recycle time of a half hour. In its present form, it is not suitable for continuous operation and was used in 30 second grinding/fuel blending runs.

The Spex mill could probably be improved by replacing the standard hammers with hammers similar to those in the Bantam mill. Replacement of the screen with 0.5 mm holes with a screen containing long, angled 0.5 mm wide slots, similar to the design in Bantam mill, would improve the performance of the Spex mill and decrease the adverse effects of long mill residence time and consequent impact heating. The fit of the screen in the Spex

Figure 22: Minimum Antimisting Concentration vs Molecular Weight for Polyisobutylene

Minimum Antimisting Concentration $C_{5\%}$ Mist (vertical axis, from 500 to 4000)

Molecular Weight in Millions (horizontal axis, 1 to 6)
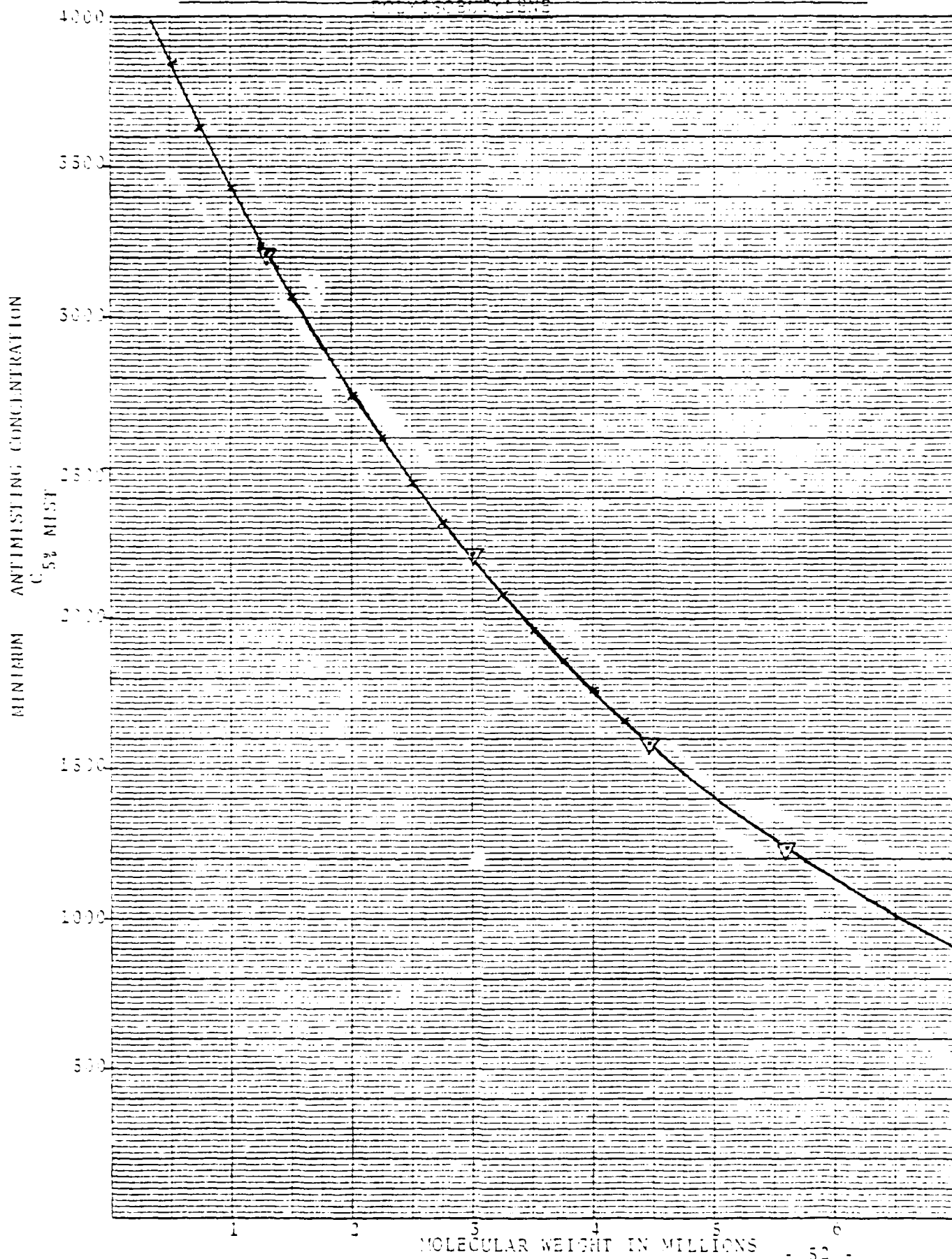
mill had enough free play to permit some polymer to bypass the
unmodified screen. A polyethylene backing insert was used to
minimize bypassing.

The cryogenic grinding/fuel blending system incorpor-
ating the Bantam mill, as modified for this project, offered
superior performance. This system, however, can only be used
with larger quantities of polymer, fuel and liquid nitrogen.
Consequently, it was used only after the antimisting data on
polymer solutions prepared using the small mill had been analyzed.

In summation, the small mill functioned well within
severe constraints, i.e., very short running time and small poly-
mer and fuel samples. This was sufficient for, and actually
expedited, the production of small lots of antimisting fuel.
The large mill had fewer constraints, due to different design
elements. These elements can be introduced into the small mill
to remove the existing design deficiencies.

2.   Effect of Polymer Molecular Weight and Chemical
Composition on the Blending Process

(a)   Molecular Weight

Tests run with the four molecular weight samples
of polyisobutylene indicate that there is no significant change
in blending requirements with increase in molecular weight.
Blending of Oppanol B-230 and Oppanol B-100 with molecular
weights of 5.6×10^6 and 1.28×10^6 respectively, with diesel
fuel required essentially the same amounts of liquid nitrogen
for cooling, used the same mill power and went into solution in
approximately the same time.

On the other hand it is clear from the data in
Tables 5 and 6 and the curve in Figure 22 that antimisting effec-
tiveness increases with increasing molecular weight. For example,
a concentration of 1100 ppm of 5.6×10^6 molecular weight polyiso-
butylene (B-230) in DF 7225 provides the same antimisting effect
as a 2200 ppm concentration of 3×10^6 molecular weight polyiso-
butylene (Vistanex L-180). Thus doubling the molecular weight in
this range reduces the required concentration by one-half.

The result is that the operational utility of the
GTA blending process is significantly enhanced by increasing mole-
cular weight of the polymer. Antimisting fuels can be blended
with significantly reduced requirements for blending and nitrogen
production equipment, and, of course, for additive.

(b)   Chemical Composition

Generally, the project work confirms earlier
results (reference (2)) indicating that the GTA process is effec-
tive in blending only those polymers which are compatible with

the solvent. Only to this extent does chemical composition affect the blending process.

In the current project the Epcar polymers co- or ter-polymers of ethylene, propylene and a small amount of unsaturated material, and the phosphazine polymer are not compatible with DF 7225. GTA was not able to prepare stock solutions of these polymers in DF 7225 using conventional blending processes nor was the GTA process effective. The other polymers which are compatible with DF 7225 were readily blended using the GTA process.

The ARCOFLO polymer may be an exception to the above rule. Conventional blending produced a solution with a significant mass of undissolved material. The solution produced using the GTA process, however, contained some particulate matter, but produced significant antimisting results shortly after preparation. More analysis of the proprietary ARCOFLO polymer is required in order to explain these results. In addition there is an indication that the ARCO polymer has a low glass transition temperature which makes efficient heat transfer during grinding a more important constraint on successful blending. This is an engineering and design problem, however, and is not a constraint intrinsic to chemical structure or composition.

3. Antimisting and Viscosity as Functions of Time After Blending

Polymer-diesel fuel solutions were tested in the antimisting fuel effectiveness tester immediately after preparation. These tests demonstrated that the solutions had antimisting effectiveness within five to ten minutes after the beginning of the cryogenic grinding/fuel blending runs (Table 5). The five to ten minutes is the time necessary for cryogrinding collection of the sample and set-up of the test. These solutions were cold, however, and it was not practical to determine viscosity using the present experimental set-up consisting of calibrated kinematic viscometers in a 100°F water bath. Viscosity determination involves bringing the solution to thermal equilibrium with bath water and time to determine and replicate viscosities.

4. Antimisting and Viscosity as Functions of Concentration

Antimisting expressed as $-\ln(\frac{P-R}{P})$, was shown in Table 5 to decrease linearly with increasing polymer concentration. This was shown for the four different molecular weight samples of polyisobutylene, RDP 10955, Natsyn AP-11, SAP-960, and ARCOFLO.

Antimisting effectiveness, expressed as the slopes of the relationships in Table 5, decreased in the following order: B-230, SAP-960, AP-11, B-200, L-130, B-100, RDP 10955, and Natsyn. These are in the order of increasing concentration required to

provide equal antimisting effectiveness. ARCOFLO presents a problem in fitting in this series owing to the uncertainty in the concentration.

At low test concentrations it was particularly difficult to measure the kinematic viscosity, although in some cases the antimisting effectiveness was well above that of neat fuel. At these low concentrations the polymer contributed little to the viscosity of the solution, and the solvent contributed strongly. These data were presented in Table 4.

These low concentration solutions exhibited viscosities too close to neat fuel to be appropriate for developing the antimisting vs concentration plots in Figures 13 through 21. Consequently, viscometry provided a concentration at the upper end of the concentration range and gravimetric dilution factors were employed to obtain the low concentration data. The extent of agreement between concentrations obtained directly from kinematic viscosities and those obtained from the dilution factors is seen in Table 4. With the exceptions of Natsyn and AP-11 the agreement is good despite the lack of viscometric sensitivity at low concentrations.

5. Stability of Antimisting Fuels

The antimisting fuels that were prepared were intrinsically stable. No special safeguards were taken to remove or exclude air or water vapor from coming into contact with the solutions. B-250, SAP-960 and ARCOFLO were stable in solution. Concentrated solutions were instantly miscible with either standard or referee grade DF 7225.

It was observed that despite the instability of the fuel, the solutions were stable. With regard to the fuel, a black substance precipitated over time. Also present in both fuels were light-scattering centers. Nevertheless, the antimisting solutions were stable in the laboratory.

As expected the severe stress associated with ejection from the antimisting spray tester severely degraded a solution of polyisobutylene in DF 7225. One pass through the spray tester reduced the molecular weight from 5 million to 1 million. In the future, this test method could be used to assess the intrinsic stabilities of candidate antimisting polymer additives.

6. Minimum Concentrations for Antimisting

During this investigation of antimisting dependence on polymer concentration, there was no evidence of a minimum or threshold concentration below which antimisting behavior disappears. It is probably more relevant to the resolution of

antimisting requirements in the field to determine the minimum
concentration associated with the desired degree of protection.

ARCOFLO exhibits a special type of threshold concen-
tration, that is the reverse of the concept of disappearance of
antimisting activity. In the region below 750-1500 ppm ARCOFLO
antimisting is a stronger function of concentration than in the
higher concentration regime. If antimisting as measured in this
project, and drag reduction effectiveness are related, ARCOFLO
may have special suitability as a low-concentration drag reduc-
tion additive. This may be of no relevance in determining the
concentration required to provide the desired degree of anti-
misting.

7.   Parameters for Optimizing the Blending Process

During this project there was an opportunity to explore
the impact of design features on mill performance and the blend-
ing process. The blending process can be optimized through the
following parameters:

(a)   Effective mill insulation and attention to heat
       transfer problems;

(b)   Knife edge cutters rather than blunt, fluted
       hammers;

(c)   Slotted screens rather than perforated ones;

(d)   Flowing fuel rather than sprayed, stirred or
       static fuel; and

(e)   Fine control of rate of addition of polymer to
       the mill.

Parameters a, b, c, and e all decrease the impact heating during
the grinding process or facilitate the removal or heat that is
mechanically generated. These parameters are especially critical
during continuous rather than pulsed operation.

The fourth parameter assures optimal contact of indivi-
dual polymer particles with a domain of neat fuel. This minimizes
coincidental fusion of active particles prior to contacting neat
fuel.

8.   Samples for Fire Resistance and Engine Performance
      Testing

Five gallon samples of B-250, SAP-960 and ARCOFLO modi-
fied diesel fuels were submitted to the project officer for
testing. The polymer concentrations in these samples were approxi-
mately 0.3%. High concentrations were supplied because lower
concentrations can be prepared by dilution of these stocks.
Referee grade DF 7225 was used because a pool of data is available
on this fuel.

V. FIELD UNIT APPLICABILITY

A. GENERAL

Contractor is required under the current contract to investigate the GTA blending process "to determine the appropriate size, weight, power requirements, etc. of a field unit."

An important parameter of any fire resistant fuel additive system for Army field use is that it requires minimal logistics support and specialized equipment. With the GTA blending process, the only additional routine continuous supply item needed for operational usage is the polymeric additive. Power is generated on-site using available fuels; liquid and gaseous nitrogen are produced on-site using the atmosphere as the source of incoming raw material. Most equipments required are in the Army inventory or are commercially available off-the-shelf items. System engineering to interface the various parts would be needed. In addition, supporting structures, necessary instrumentation for Army field use, and a few new design items will be required. There are, of course, normal maintenance and spare parts requirements.

For the purposes of this investigation the field unit will be capable of blending 50,000 gallons of antimisting diesel fuel per day with an additive concentration of 2000 ppm. Scaling upwards can be done linearly unless otherwise noted.

B. THE FIELD UNIT

A primary consideration in design of a field unit is the necessity to limit degradation of prepared antimisting fuel in handling and distribution. While several variations of blending systems utilizing the GTA process are possible, a simple "central supply method" using non or low shear pumps for antimisting fuel movement is proposed. The following design is based upon this concept.

The field unit blending system referred to hereinafter as the antimisting fuel preparation plant (AFPP) consists of items shown on Figure 23 and tabulated in Table 6. The AFPP prepares the solid additive by cryogrinding and mixing the powdered output with neat diesel fuel in the Mixing Chamber. From there it is transported by a non shear or low shear pump to holding tanks of appropriate size. The refueling of combat vehicles is accomplished from that point.

Using the 50,000 gallons per day capability as a base point, each AFPP must handle 750 pounds of additive daily. It's overall capacity is dictated by the pulverizer. The AFPP design incorporates

a pulverizer which can handle 3000-4000 pounds per day at full capacity in order to provide a safety margin against any foreseen contingencies. Liquid nitrogen requirements are conservatively estimated at 2 1/2 times the amount of dry additive treated. A liquid nitrogen plant of 1.5 tons per day is proposed.

Additive would be supplied in round form reels like cable. Each 30" O.D. reel would hold about 200 pounds of additive. The additive reel station and feeder subsystem, item 8, Figure 23, holds 2 reels which would be fed in automatic sequence so that reels can be removed and replaced when emptied in order to maintain continuous operation. Two men can load a reel into the feeder and a supply should last approximately 12 hours.

FIGURE 23

AFPP (SCHEMATIC OF ADDITIVE PREPARATION PLANT)

FROM BFTA
D.F. #2

| ① DIESEL ELECTRIC GENERATOR | ③ ④ LIQUID NITROGEN (LIN) PLANT | ⑤ ⑥ LIN STORAGE TANK |

②

ADDITIVE REEL SUPPLY

⑦

| ⑧ REEL STATION & FEEDER | ⑨ AUTO CHOPPER |

CONVEYOR PRECOOLER

⑩

ADDITIVE PULVERIZER

⑪

⑬

⑫

D.F. #2

FROM BFTA

PUMP

MIXING CHAMBER

TO HOLDING TANKS BY GRAVITY OR NO-SHEAR PUMP.
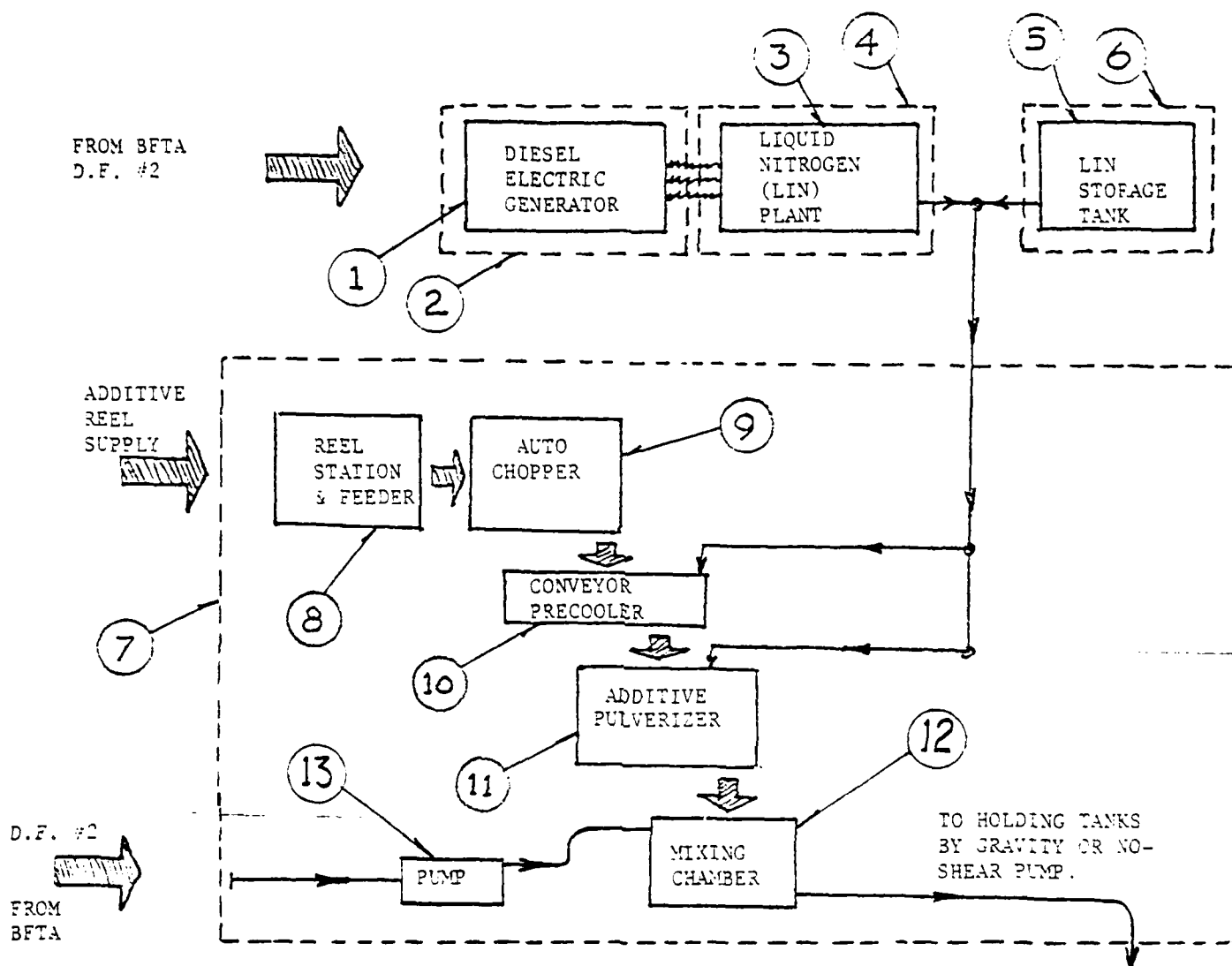
DETAILS OF VALVING; SAFETY DEVICES; CONTROLS; PANELS; WIRING; FLOW DEVICES;
AUTOMATIC FEED BACK INTERCONNECTIONS; SUPPORTING STRUCTURE OR CARRIER BODY;
SHUT-OFFS; ETC. ARE ALL OMITTED.

NOT TO SCALE

TABLE 6

LIST OF MAJOR MATERIAL FOR AEPP

NOTE: Army inventory items are indicated below where GTA is advised such equipment exists. However, exact choice must be made by the Army - to suit its needs and supply problems.

DRAWING ITEM	DESCRIPTION	SPECIFICATION	WEIGHT	SIZE
1	MEP-009B 200 KW Diesel Generator Set	MIL-STD-633E-32	10500	114" x 75" x 50"
2	SKID BASE part of item (1) above. Mounting on flatbed, trailer of Army type (1) is feasible.			
3	Liquid Nitrogen Liquifaction Plant 1.5 tons/day	SUPAIRCO DLON 150 made to MIL Specs for Army & Air Force	48000	20'W x 30'L area needed 11 - 14'
4	See (1) below for choices of plant mounting.			
5	Liquid Nitrogen Storage Tank 1500 gallon dewar	Union Carbide TR-1500	10300	15'9"H x 78"D
6	Prepared Base or platform.			
7	(1)Trailer, Flatbed 4 ton capacity	MS 52114 Type M 794 MIL STD 55/92		required (1) area 8' x 20'

TABLE 6 (CONTINUED)

DRAWING ITEM	DESCRIPTION	SPECIFICATION	WEIGHT	SIZE
8	Reel Station & Feeder estimated 2 KW	To be designed.	Estimated 150	4'W x 7'H x 5'L
9	Automatic Chopper Estimated 3 KW	Commercial type/ modification	Estimated 150	12"W x 6"D x 12"L
10	Conveyor Precooler Estimated 1.5KW	To be assembled from commercial equipment	150	4' x 6" x 6"
11	Pulverizer; Model 1W; 4KW	Pulverizing Machinery	800	3' x 2' x 4'
12	Mixing Chamber	To be designed	1800	48"O.D. x 36"
13	Mixing Chamber Feed Pump - 40 gpm	Commercial Type Electric Motor Drive	Estimated 600	5' x 3' x 4'

(1) U.S. Army has variety of vehicles, trucks, flatbeds; MIL STD 35/93; MIL-DESIGN M109A3; MIL-T 45382; MIL-T 62057; MS500032; MIL-DESIGN M109A3; MIL-T 45388B; MIL DESIGN M121A1; etc. to choose from for a mounting platform.

Items 8-13 require some 10-11 kW; this plus miscellaneous power needs indicate the choice of item 1 size is reasonable.

VI. CONCLUSIONS

A.   The GTA antimisting test apparatus and concept developed
under the current project is convenient, rapid and reproducible.

B.   Certain mist suppression polymers can be blended with
diesel fuel to form antimisting fuels in under ten minutes using
the cryogenic blending process.

C.   Among the polymers that were tested successfully are several
which indicate superior mist suppression behavior.

D.   The cryogenic blending process appears to be adaptable to
practical field operations.

VII. RECOMMENDATIONS

A. Antimisting diesel fuels should be fully evaluated as fire resistant fuels for both conventional and turbine powered land combat vehicles.

B. Criteria for a "best" antimisting additive for land combat vehicle application should be established.

C. Operational feasibility of an antimisting fuel blending system in a battlefield environment should be investigated.

D. The use of antimisting fuels for helicopters and fixed wing aircraft should be reevaluated in light of new polymer blending capabilities.

REFERENCES

(1) W.D. Weatherford, Jr., G.E. Fodor, D.W. Naegeli, E.C. Owens,
     B.A. Wright and F.W. Schaekel, "Army Fire-Resistant Diesel
     Fuel," SAE Technical Paper Series, Fuels and Lubricants,
     Hyatt Regency, Houston, October 1-4, 1979.

(2) J.C. Trippe, P. Waters and A. Hadermann, "Application of
     General Technology Application's, Incorporated (GTA),
     Blending Process to Antimisting Fuel Additives." Federal
     Aviation Administration Report No. FAA-CT-81-51, May 1981.

(3) W. Weitzen, "Method for Dissolving Polymers in Compatible
     Liquids and Uses Thereof", U.S. Patent Application Serial
     No. 117,255 (1980).

(4) Mesato Sakaguchi and Jankickh Sohma, "ESR Evidence for Main-
     Chain Scission Produced by Mechanical Fracture of Polymers
     at Low Temperature," Journal of Polymer Science: Polymer
     Physics Edition, Vol. 13, 1233-1245 (1975).

(5) Somsak Vivatpanachart, Hiroyasu Nomura, Yutaka Miyahara,
     Hisatsugu Kashiwarbara, and Masato Sakaguchi, "Detection
     and Identification of Spin-Trapped Radical Produced by Ball-
     Milling Polyethylene Powder with Nitrosobenzene," Polymer,
     Vol. 22, 132-134 (1981).

(6) Somsak Vivatpanachart, Hiroyasu Nomura, Yutaka Miyahara
     Hisatsugu Kashiwabara, and Masato Sakaguchi, "E.S.R. Study
     of the Matron of Spin-Trapped Radicals in Polyethylene in
     Relation to the Morphological Changes Induced by Ball-
     Milling.

(7) S.J. Lestz and W.D. Weatherford, Jr., "Samples of High
     Molecular Weight Polymers," Subject of letter dated 19
     June 1981, to F.W. Schaekel.

(8) H.H. Kausch-Blecken Von Schmeling, "Application of Electron
     Spin Resonance Techniques to High Polymer Fracture," Journal
     of Macromolecular Science - Reviews of Macromolecular
     Chemistry, Vol. 4, 243-280 (1970).

(9) S.E. Bresler, S.N. Zhurkow, E.N. Kasbekov, E.M. Seminskii,
     and E.E. Tomashevskii, "Investigation of Macroradicals
     formed during the Mechanical Destruction of Polymers,"
     Zh. Tekhn, Fiz., Vol. 29, 358 (1959).

(10) P.F. Waters and A.F. Hadermann, "The Instantaneous Dissolu-
     tion of Very High Molecular Weight Macromolecules."

ATE
LMED
'8